

Optimizing Anaerobic Digestion of Biomass Synergies of Fuel Cell Technologies & Organic Waste Processing

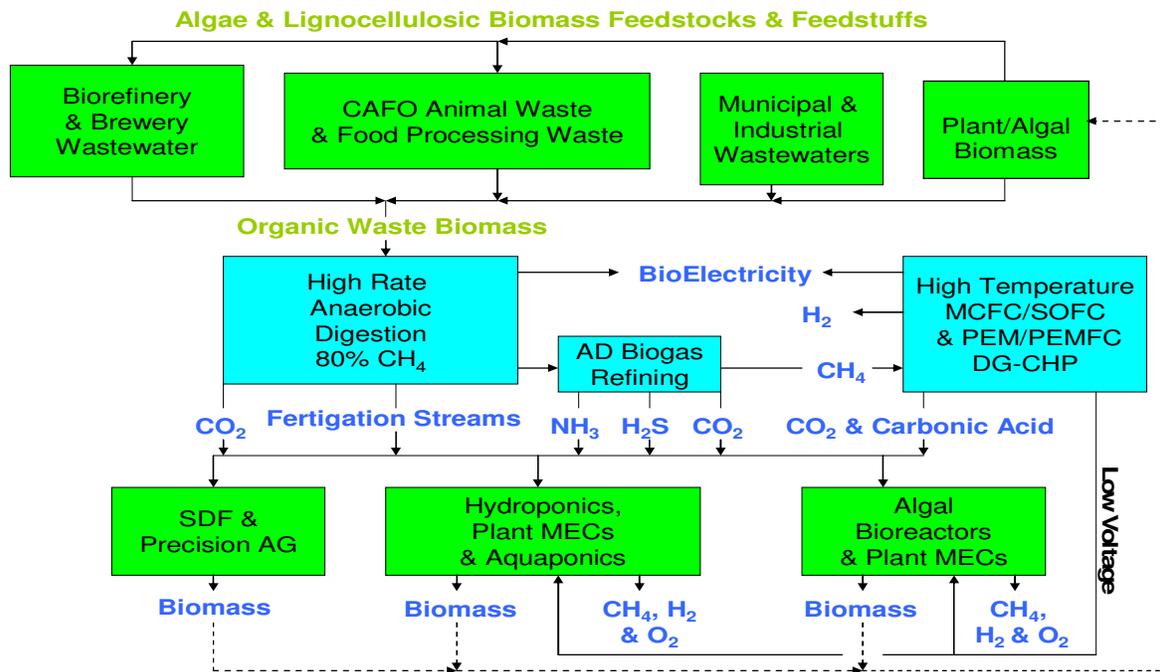


Figure 1. Closed Loop Production of DG-CHP- H₂, Biogas & Biomass.

Introduction

Methane is a greenhouse gas emission (GHGE) which is 23 times more potent than carbon dioxide. The bulk of human-produced methane emissions come from the decomposition of organic waste in landfills, ruminant digestion and manure management associated with domestic livestock production. These sources currently represent over 84% of methane emissions in the US. These GHGEs and can be dramatically reduced by improving efficiency of livestock production and organic waste management including anaerobic digestion of municipal solids and sewage ([US Emissions Inventory 2009: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2007](#)). Efficient waste management using anaerobic digestion provides an opportunity for capturing the majority of methane emissions and recycling it as a renewable biofuel. This would essentially eliminate direct sources of methane emissions resulting from organic waste processing and confined animal feeding operations (CAFOs) while simultaneously recycling biomethane and organic fertilizers. This would allow for reducing natural gas consumption and production of synthetic fertilizers for both residential and commercial applications.

Depending on the price of natural gas and synthetic fertilizers (many of which such as nitrogen compounds are produced from natural gas via hydrogen and ammonia production), the value of the crops produced by organic fertilizers can actually exceed the value of biomethane by 4-6 fold. Utilizing anaerobic digester effluents as nutrient-rich organic fertilizers for precision agriculture, subsurface drip fertigation (SDF), high density, relay cropping systems allow for more than doubling conventional crop yields per acre. This is accomplished by spoonfeeding nutrients directly to the root zones of crops in synchrony with plant growth stages (plant

maturity). In addition, SDF and conservation tilling reduces irrigation water required for producing crops by 40-60%, reduces use of synthetic fertilizers by up to 80%, and reduces fuels used to produce crops (pumping water and running farming equipment) by over 50%. This allows for reducing food and energy crop production costs by as much as 50% for integrated operations.

Comprehensive nutrient-energy management allows for efficient biochemical conversion of organic waste streams into value added resources including methane-rich biogas and nutrient-rich biological effluents for use as value added fertigation streams for closed loop production of functional foods and energy crops. This is accomplished via state-of-the-art anaerobic digestion which is a form of fermentation using native bacterium cultures. These natural decomposers efficiently convert organic waste and other forms of organic matter including portions of biomass feedstocks into biogas and organic fertilizers while eliminating emissions, pathogens, odors and insects. Organic fertilizers can then be utilized to produce functional foods and energy crops year round via controlled environment agriculture (CEA) using waste heat and low cost bioelectricity produced by integrated operations. This results in dramatically reducing production costs by internally producing biomass feedstocks which comprise up to 50-60% of inputs for lignocellulosic biorefineries, and over 70% of inputs for starch biorefineries. Utilizing organic fertilizers produced from waste resources also reduces substantial GHGs resulting from energy intensive production of synthetic fertilizers which are produced for horticultural and agricultural purposes.

From an air quality perspective, each ton of ammonia/ammonium nitrogen fertilizer requires the consumption of 40,000 cubic feet of natural gas (USDA) in order to produce ammonia. Since processing 1,000 cubic feet of gas releases 116 lbs of CO₂, a ton of ammonium-nitrogen fertilizer releases about 2.1 metric tonnes of CO₂ (NRCS; USGS). For example, producing 400 bu corn requires about 400 lbs of nitrogen fertilizer for conventional cropping systems. Since production of commercial nitrogen fertilizers is energy dependent, the more food and energy crops which are produced the more nitrogen and other fertilizers are required for production. In addition, a large portion of synthetic fertilizers for nitrogen and phosphorus currently contribute to pollution of water bodies and algal blooms via nutrient run-off. This creates a vicious cycle of inflation and pollution by combusting increasing amounts of fossil fuels in order to convert methane-rich natural gas to hydrogen and subsequently to nitrogen fertilizers. In contrast to production of synthetic fertilizers which inflate natural gas prices and do not provide micronutrients, and abundance of free organic waste resources are available for processing into value added organic fertilizers which contain a balance of essential micronutrients.

Nitrogen fertilizers are essential for efficient agricultural production of food and energy crops. However, nutrient-use efficiency is low for synthetic fertilizers and organic waste resources (such as food waste, animal waste and sewage which provide an abundance of nitrogen, phosphorus, potassium and other essential nutrients required for agricultural production) are currently underutilized. In combination with low nutrient-use efficiency for agricultural production, this results in nutrient loading, nutrient leaching and nutrient run-off which contaminate soils, groundwater aquifers and water bodies ([Erisman et al., 2008](#)). However, nutrient-use efficiency can be vastly improved by improving waste management and processing organic waste resources into value added organic fertilizers which can displace a large portion of

synthetic fertilizers. This recycling process incorporates comprehensive nutrient-energy management resulting in a dramatic increase in efficiency of agricultural and bioenergy production, e.g. providing sustainable bioeconomies while essentially eliminating environmental impacts.

Contrary to using entire crop residue biomass resources as cellulosic feedstocks for ethanol biorefining (which depletes soil organic matter), feeding a portion of crop residues to livestock and then processing animal waste into value added liquid fertilizers for conventional irrigation systems and subsurface drip fertigation (SDF) restores organic matter and essential micronutrients to the soil. The loss of micronutrients from agricultural soils due to lack of using balanced fertilizers and restoring soil organic matter, is resulting in a loss of these nutrients in food products for consumers. This lack of balanced nutrients in livestock feeds and food products affects our general health and lowers immunity to disease for both livestock and consumers.

“Twenty–eight essential vitamins and minerals play key roles in the metabolism of protein, carbohydrate, and fat, as well as in the structure of the human body (eg, vitamin K in bone matrix, calcium in bone tissue). This is also true for similar metabolic processes utilized by plants and animals including food crops, pets, and livestock. Many micronutrients are also important antioxidants (eg, vitamins C and E) or act as cofactors for antioxidant enzymes (eg, selenium in glutathione peroxidase). Several trace minerals, though not considered essential, are being studied for their roles in nutrition. Examples include silicon for bone health and vanadium for stimulation of glucose transport. Although vitamin deficiency diseases (eg, pellagra) are not widespread, suboptimal micronutrient intake is common.

Recent studies reveal that 10% to 75% of Americans take in less than the recommended dietary allowance for many micronutrients (eg, zinc, folate, iron, vitamin B₆ and B₁₂), and between 5% and 50% of Americans consume less than half the required daily allowance for many micronutrients. While what constitutes sufficient intake is controversial for some nutrients, it is clear that a surprisingly large number of people and domestic livestock are undernourished for certain micronutrients, even as they are over-nourished with respect to macronutrients. Insufficient micronutrient intake has short–term and long–term implications for disease risk. As an example, immune function is adversely affected by poor intakes of nearly every essential vitamin and mineral. Thus, diets lacking essential micronutrients may theoretically, at least, affect health over the short term by impairing resistance to viral or bacterial infection. Among longer term problems, a lack of nutrients required for DNA methylation and gene stability may increase the risk for certain cancers ([Nutrition MD](#)).”

Essentially, micronutrients increase the efficiency of metabolic processes which enhance the nutrient use efficiency of macronutrients by plants ([Yara](#)) and animals, including consumers. The abundance of balanced nutrients including micronutrients, produced from animal waste provides for year round production of high value crops via controlled environment agriculture (CEA). CEA includes hydroponic greenhouses and new generation algae photobioreactors which are predicted to annually produce over 50 times the volume of biofuels produced by conventional terrestrial crops per acre. Similar to anaerobic digestion & biogas refining, infrastructures for SDF, hydroponic greenhouses, and new generation algae bioreactors may be financed by

financial institutions utilizing tax-exempt bonds ([U.S. Treasury-IRS, 2004](#)) for solid waste disposal, and trading carbon credits for reduction of ammonia (NH₃) emissions (via lobbying efforts) and GHGE via the [CCX \(Chicago Climate Exchange\)](#).

Biogas can be efficiently desulfurized and refined into 99.9% biomethane for use as a feed for high temperature fuel cells which provide distributive generated combined cooling, heating and electrical power generation (DG-CHP). Carbon dioxide (CO₂) which is separated from biogas along with CO₂ contained in fuel cell exhaust and carbonic acid produced via condensation by heat exchangers can be utilized with fertigation streams to enhance production of closed loop biomass year round via CEA. CO₂ enrichment can increase efficiency of photosynthesis and biomass yields by up to 80% ([Bushway and Pritts, 2002](#); [Kimball et al., 2007](#)). Integrated operations which incorporate closed loop biomass and systems architecture can approach 90% total energy efficiency. This is nearly twice the efficiency of conventional gas turbine systems which operate on natural gas and produce heat, electricity and process steam via thermochemical conversion. In addition to being a renewable fuel, biomethane is considerably cleaner burning than natural gas which only contains about 80% methane. In contrast to thermochemical conversion technologies, electrochemical conversion utilized by high temperature fuel cell technologies produce electricity with heat and cogeneration of hydrogen as value added coproducts of this prime source of electricity. The result is production of grid connected power and elimination of the need for combusting natural gas and consuming electricity at integrated operations, providing unprecedented efficiencies of production via closed loop systems architecture.

Optimizing high rate anaerobic digestion allows for consistently producing 80% methane concentrations from processing of organic matter including animal waste, sewage, algae and lignocellulosic biomass feedstocks ([Ghose et al., 1979](#)). Processing equal volumes of animal waste, algal biomass and water hyacinth would allow for more than tripling biogas production and subsequent DG-CHP and cogeneration of biohydrogen (produced from biomethane). In terms of quantity and efficiency of energy produced, recent studies reveal that the efficiency of biogas production via state-of-the-art anaerobic digestion can rival that of biorefining for terrestrial crops ([Gunaseelan, 2009](#)). Energy efficiencies for processing aquatic plant biomass such as algae and water hyacinth which require fewer inputs and grow faster than terrestrial crops are expected to provide even greater energy efficiencies. Thus, anaerobic digestion provides an immediate alternative to processing advanced biofuel feedstocks consisting of lignocellulose and lipids in an efficient and cost effective manner while providing value added organic fertilizers for closed loop food and energy crop production. This subsequently provides a bridge for development of economical pretreatment and biorefining technologies required for sustainable production of liquid biofuels and a variety of high value coproducts at integrated biorefineries.

Achieving 80% methane concentrations in biogas is primarily accomplished by balancing nutrient ratios (including a 30:1 carbon to nitrogen ratio) for microbial cultures for either mesophilic or thermophilic environments ([Ghose et al., 1979](#)). In addition, uniform reduction of particulate size for substrates via a combination of mechanical grinding and economical ultrasonification/electromagnetic force pulse allows for increasing surface area of organic matter, thus maximizing enzymatic and microbial access. Regulating digester pH, electrical

conductivity, temperature, providing a continuous in-flow of fresh substrates, agitation, removal of excess nitrogen, retention of bacteria and addition of biocatalysts can maximize solids destruction for anaerobic digestion. This subsequently results in maximizing methane concentration, increasing volume of biogas produced, and reduction of hydraulic retention time (HRT). Optimizing HRT for anaerobic digesters is critical for reducing capital investment and environmental footprint of anaerobic digesters and biogas processing facilities.

Excess protein (source of nitrogen) in organic substrates can result in production of excess ammonium cations and subsequently ammonia gas during anaerobic digestion. The ammonium cation (also known as ionized ammonia due to its electrical charge) is a positively charged polyatomic cation of the chemical formula NH_4^+ . It has a formula weight of 18.05 and is formed by the protonation of ammonia (NH_3). Avoiding production of excess nitrogen during anaerobic digestion is most efficiently accomplished by balancing nutrient ratios (particularly the C:N ratio) and also by implementing continuous out-flow of biological effluents. Routine removal of anaerobic digester effluents results in efficiently and cost effectively removing ammonium cations which are suspended in the effluent. This reduces protonation during enzymatic hydrolysis of substrates and subsequent conversion of acetic acids to methane. Reducing protonation reduces production of ammonia which impairs functioning of methanogenic bacteria. It also preserves the nitrogen component of organic matter in liquid form for use as a value added fertilizer in fertigation streams. Ammonium is the preferred form of nitrogen for absorption by most plant species and is ideal for use with closed loop production of functional foods and energy crops. Continuous inflow and outflow is one of the most efficient and economical means of processing organic waste and providing agitation. In addition, the induced blanket reactor (IBR) technology utilizes an auger positioned in the middle of the upflow digester with a septum at the top of the digester for retaining bacteria. Preventing the loss of bacteria in effluents speeds microbial processes and assists with reducing HRT for digesters.

In regards to processing biogas containing ammonia, current research is focused on development of biogas and ammonia solid oxide fuel cells (SOFC). Organic waste and biomass offer extremely high potential as carbon-neutral fuel sources for power generation. Technology Management, Inc (TMI) proposes to demonstrate how ammonia contaminated biogas produced from wet biomass can be converted into useful electricity and heat by commercializing SOFC applications. TMI proposes to operate a SOFC system on ammonia contaminated biogas directly as a renewable fuel and produce clean, on site electricity, thereby simultaneously removing harmful pollutants while reducing operating expenses and dependence on conventional grid-based electric power ([USDA & TMI, 2006](#)). Ammonia SOFCs could eventually eliminate biogas reforming which is currently required for molten carbonate and phosphoric acid fuel cells. However, production of H_2S needs to be reduced in order to avoid sulfur poisoning. This can be accomplished by optimizing efficiency of digestion and subsequently removing residual H_2S in biogas via adsorbent beds or other means. SOFCs operate at higher temperature ranges (650-1,000 °C) than either MCFCs or PAFCs, use inexpensive ceramic materials for construction, and are generally more efficient than other fuel cell designs. Higher operating temperatures eliminate the need for using precious metal catalysts and capital intensive reforming for a variety of fuel feeds ([Patel & Petri, 2006](#)).

Though the high rate mesophilic IBR digester can provide as little as 4-5 days HRT for processing dairy waste with solids loading rates of 8-10%, high solids (20-45% loading rate) thermophilic digester technology developed by NREL allows for processing a wide variety of typically hard to digest substrates including crop residues, animal hair, animal offal, sewage, and municipal green waste with a HRT of 16-20 days. The five fold increase in solids loading rate for the HSAD compensates for the longer HRT time. In addition, the thermophilic environment of the HSAD eliminates 99.9% of pathogens in biological effluents and sludge, and reduces HRT time by up to 20%. The mesophilic IBR technology has a solids destruction rate of 45% compared with 65% for the thermophilic HSAD technology. The HSAD technology converts 85-90% of carbon contained in mixed substrates to methane and carbon dioxide while consuming less than 15% of total energy produced by the digester. Low operating cost and high methane concentrations, 20-45% solids loading rate for a variety of hard to digest feedstocks, 65% solids destruction rate, elimination of 99.9% of pathogens, all contribute to making the thermophilic HSAD technology appear to be extremely efficient and versatile.

Over a period of time, sand and the undigested portion of solids builds up in anaerobic digesters. In order to alleviate this problem and insure optimal efficiency, *in situ* sand and sludge removal technology has been successfully utilized with IBR technology. This *in situ* removal process could potentially be utilized with HSAD technology.

Proprietary biocatalysts have been developed for mesophilic digesters. One in particular has increased solids destruction and subsequent methane production by 25%. This particular biological product consists of five main components that function synergistically to improve the performance of biological treatment of organic solids, wastewater, and gaseous wastes, as well as to control undesired biofilm. These components are:

- Enzymes that hydrolyze organic solids and facilitate the transport of soluble organics into active cells of microbes
- Fatty acids that favor the growth of methanogens and the methanogenic breakdown of organics
- Biosurfactants for processing complex organics, particularly helping the digestion of fats and oils and also minimizing production of foam and odor release
- Essential mineral nutrients required for microbial growth
- Chelating agents that keep the inorganics in suspension and prevent scaling

In rigorous bench tests, biocatalysts have improved biodegradation rates of aerobic and anaerobic bacterial cultures, minimized the reduction of sulfate to hydrogen sulfide, minimized the release of ammonia, and controlled production of undesired biofilms. In particular, the rate of solids destruction and the generation of the valuable degradation end product – methane gas – increased when the biocatalyst was added to the influent at only 0.5 ppm. The biocatalyst increased the rate and extent of the two key reactions in anaerobic microbiological treatment: solids hydrolysis and methane generation by almost 25% (Rittmann et al., 2005). The positive results produced by the validation of this particular biocatalyst confirm the importance of efficiently processing organic substrates and optimizing nutrient ratios which may provide similar results as those provided by proprietary biocatalyst. Though the biocatalyst was bench tested for mesophilic applications, subject to validation, it may provide similar (though probably

less productive results) for thermophilic applications which already achieve higher solids destruction and reduce HRT by 20% relative to substrates utilized.

Improving efficiency of anaerobic digestion also improves the quality and performance of processing biological effluents into value added fertigation streams. Injection of urea-sulfuric acid into fertigation streams minimizes biofilm and scaling in precision irrigation systems, particularly subsurface drip fertigation (SDF) and CEA applications. When utilized with high density relay cropping systems, nutrients can be spoon fed to roots of crops in synchrony with plant growth stages (maturity). This results in more than doubling conventional crop yields while eliminating nutrient run-off and subsequent pollution. For year round CEA production of aquatic plant species such as algae and water hyacinth (which reproduces and grows almost as fast as algae), the rate of biomass production via extended photoperiods, CO₂ enrichment, and precision agriculture can be increased exponentially in comparison with seasonal terrestrial crops.

Accurate & Economical Nutrient Sampling & Sensing

Since it is a type of fermentation, efficiency of anaerobic digestion depends on precision management. Optimizing nutrient ratios allows for maximizing efficiency and concentration of methane-rich biogas. In addition, from an ecological perspective organic waste processing and precision agriculture provides comprehensive nutrient-energy management which essentially eliminates nutrient leaching, nutrient-run-off, and dramatically reduces GHGs. Accurately sampling and testing organic waste substrates to achieve an optimal balance of carbon, nitrogen and essential macro- and micro-nutrients for anaerobic digestion is necessary for efficient agricultural production of both food and energy crops. Accurate nutrient-chemical sampling and sensing in conjunction with comprehensive nutrient-energy management simplifies conditioning of nutrient-rich biological effluents for use as value added organic fertigation streams. Fertigation is a form of chemigation in which fertilizers and specialty fertilizer products are delivered in irrigation. Chemigation is a tool of precision agriculture which is considered a best management practice (BMP) by USDA.

Unfortunately, conventional chemical extraction methodology was developed several decades ago. Despite several advances in chemistry, soil and water media sampling and testing has not significantly changed except for a wide variety of chemical solutions which have been developed for extraction according to specific soil types and target elements. Between four to ten chemical extractions are currently required to obtain an incomplete nutrient analysis of an individual soil sample using conventional testing methodology. For example, sulfur, a secondary macronutrient which is essential for plant production, is simply not detectible via conventional chemical extraction and sensing processes.

Conventional nutrient sampling and sensing is a mechanically intensive process that requires physical collection of representative samples, transportation to the lab, air or oven-drying, grinding, weighing, and multiple extraction steps with specialized equipment required for each process. Furthermore, the results from various chemical-extraction tests do not account for the dynamic nature of soil and water chemistry, but rather provide only a “snapshot” of the status in the medium at the time of sample collection.

The influences of dynamic soil processes and complex soil biochemistry such as those exhibited by mineralization, immobilization, nitrogen fixation from crop rotations with legumes, nitrification and denitrification, dissolution of soil solids, and ion exchange from soil colloids (all of which influence nutrient bioavailability) are not accurately reflected using conventional chemical extraction and sensing processes. Conventional soil tests which measure the effect of time on the availability of N, P, & K can take up to two to three weeks and cost up to \$50 for each individual nutrient test. Furthermore, results obtained from conventional sampling and chemical extraction indicate what is transpiring under a set of specified lab conditions and reveal little about what is occurring under actual field conditions. Values for secondary macronutrients Ca, Mg, and S obtained by chemical extraction are often inaccurate, and therefore tests for these nutrients are seldom conducted. This is a critical failure of conventional processing since these essential nutrients, which are usually limiting for crop production, are responsible for enhancing nutrient-use efficiency (NUE) for N, P & K.

Obtaining accurate values for micronutrients Fe, Zn, and Cu, which can also significantly affect crop yields, can be problematic utilizing conventional chemical extraction processes. A comprehensive conventional soil/organic matter test including data for most essential nutrients, salts and heavy metal contaminants contained in a single media sample can cost well over \$100 using the multiple chemical extraction processes required for conventional soil testing. Hence, comprehensive nutrient analysis is seldom requested by producers due to economic reasons. Less than one fifth of US forage croplands are soil sampled. The result is inefficient management of nutrients via conventional media sampling and nutrient evaluation of soils, organic waste, water, and plant tissue. This dilemma has both economic and environmental consequences.

Heterogeneous substances such as manure piles and other types of organic waste which contribute largely to nutrient loading require testing several random samples in order to obtain a representative nutrient analysis of the material. In addition, numerous soil samples are normally required from within a single agricultural field in order to account for soil spatiality and obtain useful soil analyses prior to land applications of organic waste and/or synthetic fertilizers. The wide variety of soil types, which exist in the US and around the world, also mandates use of several different chemical extracts since no single extract will work on soils of different types (e.g. acid soils vs. calcareous soils) for conventional soil testing.

“Variations in soil testing results have been documented through the submission of duplicate, blended samples to laboratories in the west (Davis et al., 1999; Lorbeer et al., 1999; Koenig, 2003). Although in specific instances this variation can be attributed to differences in extraction methodologies, variation among labs using identical procedures does exist (Miller and Kotuby-Amacher, 1997; [Miller, 2006](#)).” Interestingly, variation of test results among lab technicians is usually greater than the variation exhibited among individual labs (Miller, 2007). Due primarily to the lack of quality control and inconsistent lab procedures, the same soil or organic waste sample can vary by over 50% using conventional chemical extraction methodologies (Quaggio et al., 1994; [Skogley et al., 1996](#)). There is currently a 25% mean variation among soil tests for labs in the western US ([Miller, 2006](#)). These data illustrate a serious problem with the accuracy and reliability of contemporary soil and water media tests. The inaccuracy, inconsistency, and relatively high cost of conventional chemical extraction results in a general lack of nutrient

testing by many livestock producers, agricultural producers, food processors and industrial manufacturers. This is particularly true in regards to testing soils, water, and efficiently managing industrial/organic waste materials prior to land applications. Many of these waste materials are rich in valuable nutrients. If processed and applied properly, the nutrients contained in organic waste can economically reduce the need for energy intensive manufacturing and purchasing of synthetic fertilizers while simultaneously reducing pollution of soils, water bodies, and the atmosphere via reduction of particulate matter (PM) and GHGE.

In order to circumvent deficiencies in current methodologies for nutrient sensing, various approaches are being used. “N fertilizer recommendations for corn production are usually estimated on the basis of a realistic yield goal, which is multiplied by 1.2 to calculate the pounds of N required per acre, less any adjustment for N derived from other sources, such as manure or legumes. A yield-based recommendation may have merit on a long-term basis, but under- or over-fertilization is apt to occur in any given growing season, since soil N availability is not taken into account. Insufficient application of N can have serious economic consequences for the farmer, whereas excessive fertilization increases the risk of environmental pollution.”

“Environmental concerns that excessive N fertilization may contribute to nitrate enrichment of ground and surface water has stimulated interest in soil testing in order to improve the accuracy of N fertilizer recommendations for corn and other crops. For many years, a preplant nitrate test (PPNT) has been used in western Canada and the Great Plains region (including the Mississippi River basin) to account for carryover of mineral N from previous cropping. A more recent option is the presidedress nitrate test (PSNT), in which case soil sampling is postponed until corn is 6 to 12 inches tall, so as to estimate plant available nitrate as closely as possible to peak uptake by the crop. If the test indicates less than 20 to 30 ppm of nitrate-N in the surface 12 inches of soil, supplemental N is applied as a sidedressing. The PSNT has been recommended more widely than the PPNT in the eastern U.S., but usage has been limited by the need to collect soil samples during the growing season, when farmers are occupied with many other tasks. Fertilization must be postponed until after testing, which can lead to crop N deficiency if adverse weather conditions prevent sidedressing. Hence, neither test is currently recommended by several leading soil scientists and agronomists. Besides logistical problems, an inherent limitation with soil testing for nitrate arises from the dynamic nature of N-cycle processes, most of which affect soil nitrate concentrations. Ideally, a soil test for N would estimate a labile (readily undergoing change) organic fraction that supplies the plant through mineralization. This approach would have an advantage in that soil test levels would depend on fewer N-cycle processes. Thus, these levels would be less prone to temporal and spatial variability, so that N availability could be potentially predicted on the basis of a one-time test, regardless of soil type or management. Further, the time of sampling would be much less critical than with nitrate, and samples could be stored for later analysis (Mulvaney, 2001).”

Many advances in technology have been developed for increasing accuracy of media sampling and sensing. These include ion exchange resins, direct sensing technologies, greater knowledge of soil biochemistry, and computer science, all of which can aid in processing soil test data, understanding complex soil biochemistries, and forecasting subsequent fertilizer recommendations (Murphy, 2007; Skogley, 2007).

In addition to responsible nutrient sampling and sensing of soil, organic waste, and water, accurate nutrient sampling and sensing of plant sap/tissue is essential for comprehensive nutrient-energy management. Plant sap or foliar analysis is the gold standard for determining nutrient requirements for plants. However, similar to soil analysis, there is currently a lack of universal standards for plant sap/foliar sampling and analysis. It appears obvious that approaches such as those listed above for soil and plant nutrient sampling and sensing have serious drawbacks and improved technology is required in order to resolve current inadequacies of conventional soil and plant tissue testing. This is essential in order to improve NUE for agricultural production.

Soil nitrogen tests and other nutrient tests integrated with plant analysis can help farmers improve their net farm income (Babcock and Blackmer, 1994; Shortle et al., 1993; Bosch et al., 1994), and simultaneously reduce pollution. Ion exchange resin technology which has been utilized commercially in various industrial processes for over 80 years, shows much promise for use as a universal standard for nutrient sampling and sensing for both soils and plants. Ion exchange resins are widely used in separation, purification, and decontamination processes. The most common examples are water softening and water purification. In regards to resin types, the substances are often referred to as adsorbents, which are commercially available as inorganic ion-exchangers, carbonaceous resins that exhibit hydrophobic sorption of organics, cellulosic exchangers, liquid ion-exchangers, membranes, fibrous exchangers, films, powders, foams, and capillaries (Dorfner, 1991). Ion exchange resin capsules designed for use in agriculture adsorb only those forms of nutrients, toxins and contaminants which are available for plant absorption. When used serially, more or less on a weekly or biweekly basis, chemical/nutrient sensing of both cations and anions will reflect the dynamic nature of complex soil biochemistry. Resin capsules function as universal nutrient accumulators, simultaneously adsorbing available forms of each nutrient/ion present in the soil. Finally, the resin capsule can be used in soils of all types to provide a means of standardizing soil/media testing worldwide.

Similar to the method in which plants absorb nutrients, synthetic ion exchange resins act as ion sinks, responding to the flux of ion diffusion in soil and water over time. Ion diffusion is a primary mechanism that controls NUE via absorption at the plant root surface. Several nutrient ions are particularly sensitive to diffusion for availability to plants, especially K, P, S, & NH₄ (Skogley, 1994). Other nutrient ions are at least partially regulated by diffusion toward the plant root. Values for Ca, Mg, and S obtained from resin capsule accumulation reflect the bioavailability of these ionic nutrients and are included in routine tests. This allows for addressing crop deficiencies and imbalances of these essential plant nutrients which are often ignored when using conventional chemical extraction methodologies. In addition, ion exchange resin capsules accurately reflect the contribution of labile organic fractions in the soil as they undergo various biological transformations including mineralization and immobilization prior to releasing nutrients for plant absorption.

For use in the field, resin capsules can be strategically located in various soil types, manure piles, and wastewaters to provide data on nutrient availability under existing conditions. Though numerous resin systems have been used for soil and environmental studies (Skogley & Dobermann, 1996), currently only two resin technologies have been commercially developed for nutrient analysis. These are mixed-bed resin capsules ([Skogley et al., 1996](#)) and resin membrane

probes. Both simulate nutrient absorption by plant roots. These resin technologies are currently available for commercial use for evaluating bioavailability of nutrients in soils (in-situ) or in labs via fresh soil, organic matter, or water media samples. Strict quality controls and lab protocols should be implemented to insure consistency of nutrient samples and uniform lab test results when using ion exchange resin capsules, particularly for *in situ* applications ([Skogley et al., 1997](#)).

Ion exchange resin capsules contain a mixture of equal amounts of cation resin and anion resin (referred to as mixed-bed resin capsules). The resin types are strong-base and strong acid, and initially saturated with H⁺ and OH⁻ ions. These characteristics assure that the capsules have an affinity for all other ions (except bicarbonate) in the surrounding medium and that they will function as a sink (or ion accumulator) during the monitoring/testing period. The capsules are spherical, with a rigid surface that is porous and of uniform area. These physical properties provide a system in which the area of contact between the soil and the resin capsule is known and remains constant during the extraction period. Under these controlled conditions, the quantity of each solute accumulated in the capsule during a specified time is dependent upon solute concentration and rate of solute diffusion to the sink (Yang & Skogley, 1992). Nutrient adsorption by these capsules is simultaneous and independent for each ionic species (Yang, et al., 1991). Solute concentration and rate of solute diffusion are dramatically influenced by soil moisture level, temperature, and pH, so as these conditions vary over time, this will be reflected in the analytical results of resin capsules.

The quantity of resin in the ¾ inch diameter capsule is large enough to act as an infinite sink for ions for extended periods of time (over 2-4 weeks) in most media. Hence, ion exchange resin capsules have a much larger adsorption capacity than resin membrane probes and can be used over longer periods of time for *in situ* applications. Capsules also provide the flexibility for inserting at various soil depths extending deep within the vadose zone (between the root zone and the water table) using commercially designed tubes for this purpose. The resin capsules are then simply retrieved from a soil access system by detaching them from the inner tube which was used to originally lower the capsule into place. This allows for convenient monitoring of nutrient leaching and contaminants in soils and groundwater aquifers. Once retrieved from the test media, the capsules are rinsed off with deionized water to remove any adhering soil particles prior to elution.

Ion exchange resin capsules and membrane probes are based on the same scientific principles and function similarly. Either will more accurately and efficiently measure ion diffusion and the dynamics of soil chemistry than conventional chemical extraction soil tests. There are, however, distinct differences. Unlike resin membrane probes, resin capsules are designed for use with inorganic nutrients and other ions in soils, water or other media. In addition, specialized capsules are available for measuring organic solvents or gases in various media. Resin capsules can be used to collect charged atoms and molecules from chlorinated industrial solvents, hydrocarbons such as gasoline and other petroleum products, pesticides, organic heavy metal complexes and soil humics for both agricultural and environmental purposes.

Due to the size, design, and relatively small capacity of the resin membrane probe, its use is generally restricted to the first four to six inches of soil or organic matter. Resin probes are

designed for short term evaluations, from 24 hours to about a week. Length of testing periods depend on nutrient concentrations, CEC (cation exchange capacity), type of cropping and nutrient management systems utilized. Due to the dynamic nature of ion diffusion, longer-term evaluations are usually more accurate than short-term evaluations for determining bioavailability of nutrients. Unlike the resin membrane probe, longer adsorption periods utilized for the resin capsule provide sufficient detection levels for evaluating sorption rates in the soil solution for nutrients such as ammonium, borate, chloride, calcium, magnesium, and molybdenum ([Western Ag Innovations](#); Schoneau, 2007). As more time is allowed for determining the flux of ion diffusion in soil solutions, the greater will be the ability to accurately measure the influence of dynamic soil processes. The resin probe technology requires separate probes for collecting cations or anions, plus a third one for heavy metals, while the mixed bed resin capsules simultaneously adsorb all ionic nutrients, toxins, heavy metals and other contaminants.

The top 4-6 inches of the soil is where the majority of organic matter conversions (e.g., mineralization and immobilization) occur. This is where shallow rooted plants, such as common turf and pasture grasses, obtain their nutrients and water from surface irrigation and fertilizer applications. Sampling only this portion of the soil, however, merely provides a small glimpse of the entire root zone profile. For plants with deeper roots such as corn or legumes (alfalfa and soybeans), the most accurate soil analysis for plant nutrients and contaminants is obtained through extended evaluation periods at various depths in the soil. This can be accomplished via ion exchange resin capsules with the aid of convenient soil access systems described above. This deeper soil analysis is critical for determining water and ion percolation rates and monitoring leaching of contaminants into the vadose zone and into groundwater tables. Due to their design and flexibility, ion exchange resin capsules are better suited than resin membrane probes for testing in conjunction with various irrigation technologies such as sub-surface drip fertigation (SDF). SDF systems emit nutrients as deep as 12 inches or more below the soil surface, depending on design. Cultivation will disturb the soil matrix, making it necessary to take deeper soil samples, down to about one or two feet or more, on a regular basis in order to accurately sense soil nutrients.

Unlike the resin membrane probe, the resin capsule can be conveniently utilized to monitor streams, lakes, wells, and groundwater tables. “The capsule can be placed directly in the water at the desired location and then stabilized. One example is to suspend capsules at desired intervals on a cord, use a weight on the bottom of the cord, and drop the set-up down a water-filled borehole. Periodic retrieval and analysis of capsules will allow for the determination of the solute chemistry, and any chemical stratification, in the borehole. Because ion accumulation is diffusion-dependent (even in free water systems) quantities of chemicals accumulated during placement or retrieval of the capsules will not invalidate results obtained during long-term studies. For studies in flowing waters, capsules may be constrained in plastic cages or other devices that allow for free movement of water around the capsule. Groundwater studies may involve use of perforated tubes (to allow normal water flow) installed to desired depths and into which capsules can be inserted and retrieved periodically. This type of installation, if used at intervals throughout riparian areas, will allow detection, and identification of sources of chemicals entering stream systems ([Skogley et al, 1996](#)).”

Lack of technology transfer of ion exchange resin capsule and the diagnostic recommendation integrated systems (DRIS) technologies has been due primarily to reluctance of the soil and plant tissue testing industry to adopt new technology. In addition, there is a strong need for interactive software tools to interpret data, and enhance nutrient management via accurate prediction of fertilizer requirements by integrating soil and plant sap/tissue analysis. Validation of resin capsule correlations with plant root uptake/absorption will allow for integration of resin capsules and DRIS via interactive web-based nutrient management software.

All data collection will occur from uniform soil samples extracted and sensed via strict lab protocols which have previously been developed. The scientific characteristics and modes of action of resin capsules have been extensively studied and proven under lab conditions (Dorfner, 1991; Yang et al., 1991; Yang & Skogley, 1992; Skogley, 1994; Skogley and Doberman, 1996; [Skogley et al., 1996](#); [Skogley, et al., 1997](#)). The following are examples of nutrient concentrations obtained from chemical extraction of ion exchange resin capsules using conventional equipment for sensing and analysis of elution:

Table 1. Ion exchange resin capsule analysis for 48 hour adsorption period in a lab environment using standard autoanalyzer equipment.

Primary Nitrogen Ions	Method DL ug/mL	Solution ug/mL	ug/cm ² (ppm)	Conventional Extractable Data
NO₃	0.002	0.16	23	20?
NH₄	0.002	0.04	4.6	4

(Data extrapolated in 2007, accuracy of data needs verification)

Table 2. Ion exchange resin capsule analysis for 48 hour adsorption period in a lab environment using standard ICP equipment.

Elements	Method DL ug/mL	Solution ug/mL	ug/cm ² (ppm)	Traditional Saturated Paste Results ug/mL	Conventional Extractable Data
S	0.1218	9.4927	41.6346	6.0	X - S 18
Zn	0.0091	0.0174	0.0762	< 0.1	DTPA 2.2
Mg	0.0175	12.1660	53.3596	15.0	X - Mg 470
Ca	0.0105	61.0131	276.3732	43.0	X - Ca 2800
Fe	0.0013	0.6279	2.7538	4.5	DTPA 68
B	0.0034	0.0433	0.1898	< 0.1	Hot Water 0.6
Cu	0.0004	0.0084	0.0369	< 0.1	DTPA 1.4
Mn	0.0343	3.4859	15.2892	1.5	DTPA 110
Na	0.0493	1.3045	5.7215	15.5	X - Na 15
K	1.9445	20.5772	90.2509	10.0	X - K 225
Al	0.0034	0.9382	4.1150	5.4	X - Al < 0.1
P	0.0638	1.4503	6.3610	1.8	Olsen 22
Mo	0.0588	0.0028	0.0124	< 0.1	X - Mo < 0.1
					pH 5.9
					OM 3.4
					EC 0.4

(Data provided by Byron Vaughan of [AgSource Cooperative Services/Harris Laboratories](#), 2007)

Comparisons among nutrient supply rates for ion exchange resin technology with conventional chemical extractions, and plant absorption reveal the following correlations which confirm the accuracy of the ion exchange resin technology:

Table 3. Correlation of Ion Exchange Resin Data with Conventional Chemical Extraction & Actual Plant Absorption

Ionic Species Sensed with Ion Exchange Resins	Associated Ionic Compounds	Correlation (r^2) with		References
		Conventional Extraction	Plant Absorption	
Nitrate	NO_3^-	0.69	0.86	Qian & Schoenau, 1995
Phosphate	PO_4^{3-}	0.57	0.71	Schoenau <i>et al.</i> , 1993
Sulfate	SO_4^{2-}	0.73	0.98	Greer & Schoenau, 1994
Borate	BO_4^{3-}	0.79		Greer & Schoenau, 1994
Chloride	Cl^-	0.81		Greer & Schoenau, 1994
Potassium	K^+	0.87	0.68	Quian <i>et al.</i> , 1996
SAR	Cation	0.95	N/A	Greer & Schoenau, 1996
Calcium	Ca^{2+}	0.68		
Magnesium	Mg^{2+}	0.68		
Ammonium	NH_4^+			
Chromium	Anion	0.98	0.99	Tejowulan <i>et al.</i> , 1994
Manganese	Mn^{2+}	0.50	0.68	Tejowulan <i>et al.</i> , 1994
Iron	Fe^{3+}	0.61	0.71	Liang & Schoenau, 1995
Nickel	Anion	1.00	1.00	Liang & Schoenau, 1995
Copper	Cu^{2+}	0.78	0.75	Tejowulan <i>et al.</i> , 1994
Zinc	Zn^{2+}	0.83	0.74	Tejowulan <i>et al.</i> , 1994
Cadmium	Anion	0.98	0.98	Liang & Schoenau, 1995
Lead	Anion	0.97	0.98	Liang & Schoenau, 1995
2, 4-D amine	Anion	0.98	N/A	Szmigielska & Schoenau, 1995
Metsulfuron	Anion	N/A	0.98	Szmigielska <i>et al.</i> , 1998
Glucosinolates	Anion	0.98	N/A	Szmigielska <i>et al.</i> , 2000

The correlations between the ion exchange resins and chemical extraction can be utilized to accurately estimate fertilizer recommendations for macronutrients such as N, P, K, Mg, S & Ca. In the future, web-based nutrient manager software can be utilized to forecast fertilizer recommendations utilizing tissue analysis via sap analysis and DRIS (diagnostic recommendation integrated system) nutrient ratio indices integrated with ion exchange resin capsule technology ([Uni-Sphere™ Ion Exchange Resin Capsules](#)).

In addition to sensing of nutrients in soil, organic waste, and water, accurate plant tissue analysis is essential for efficient nutrient-energy management. Foliar diagnosis can reveal nutrient imbalances, insufficiencies, and excesses. However, information pertaining to fertilizer requirements, or even plant response to applied fertilizer, cannot be generated solely by way of foliar analysis due to non-nutritional factors such as temperature, fertilizer placement and tillage

practices. Diagnosis of sap and leaf material may reveal, for example, that a plant contains a suboptimal level of P, but one cannot determine from this information how much P fertilizer to add, nor necessarily by how much the plant will respond to added P. Ideally, foliar diagnosis can provide a source of information that, when coupled with accurate soil test data via resin capsules, knowledge of field history, weather conditions, and experience, will allow the agriculturist to more accurately predict nutrient requirements via determination of optimal nutrient ratios. For this purpose, integration of resin capsules and (DRIS) foliar (Walworth and Sumner, 1988) and sap indices can be utilized for development of innovative nutrient-energy management software. Such software could enable one to make intelligent decisions and recommendations with unsurpassed efficiency and accuracy.

Plant sap and foliar analyses are useful tools for assessing plant nutrient status only if adequate procedures are available for making diagnoses from analytical data. Because of the dynamic nature of sap and foliar composition, which is strongly influenced by aging processes as well as interactions affecting nutrient adsorption and distribution, sap and foliar diagnosis can become complex exercises. The DRIS was developed by Beaufils (1957, 1971, 1973) as an objective means of coping with the difficulties inherent in diagnostic procedures. It has long been recognized that nutrient concentrations (nutrient mass/total dry plant mass) change markedly as plants age. Though genetic variations exist, in general research reveals that foliar concentrations of N, P, K, S, Cu, Zn and B tend to decrease during plant aging. In contrast, Ca and Mn concentrations tend to increase, although declines have been noted in early and late stages of growth in some crops. Mg increases or remains constant (Beeson and MacDonald 1951; Rominger et al. 1975; Sumner 1985). This makes the stage of growth at sampling an important consideration. The dynamic nature of plant sap and tissue nutrient composition imposes severe limitations on the use of foliar analysis for diagnostic purposes (Bates, 1971; Bouma, 1983). Critical nutrient value or sufficiency range systems generally depend on diagnostic norms derived from plant tissue of a specific age and categorize plants as healthy or unhealthy based solely on nutrient concentration (nutrient mass/dry plant mass). Thus the stage of growth of the sampled plant is a prime concern. For this reason, diagnoses based on the use of such standards are usually applied only to plant samples harvested within narrowly specified stages of growth. However, the use of ratios reduces diagnostic problems induced by variations in sampling time without requiring an estimation of plant maturity. This is accomplished by accurately estimating the physiological age of the plant, a critical component of accurate diagnosis in practice (Walworth and Sumner 1987, 1988).

One means of coping with the dynamic nature of foliar composition, as it pertains to diagnosis of the status of mineral nutrition in crop plants, is exemplified by the DRIS. In 1973, Beaufils reasoned that if N, P, and K concentrations (relative to dry matter) all decrease during aging, then ratios N/P, N/K, and P/K (or their reciprocals) should remain fairly constant. Similarly, because Ca and Mg concentrations usually increase during aging, a quotient formed from these two nutrients (Ca/Mg or Mg/Ca) should also produce a constant value. Furthermore, products of two nutrients, one of whose content relative to dry matter decreases and the other increases with time, (N x Ca, for example) should also be fairly constant. Research reveals that these concepts have proven correct within moderate ranges of age. Hence, the strengths of the DRIS for evaluating nutrient balance using plant nutrient ratios, including reduced effect of tissue age and placement, have been demonstrated for commercial use (Walworth and Sumner, 1987, 1988). In

addition, regular evaluation of plant sap provides crucial real time data for delivery of nutrients directly to the root zones of crops via SDF in synchrony with plant growth stages.

The versatility of nutrient ratios is enhanced when expressed both as ratios with DM (dry matter) and with other nutrients. DM is in fact a measure of C, H, and O in plant tissue, which are also essential elements though often not treated as such. The DM forms of expression (N%, P%, and K%) are much more closely related to age than are expressions in the form of nutrient ratios. Similarly, coefficients of variation for nutrient ratios are much smaller than are those for N, P, and K on a DM basis, indicating that by calculating ratios the influence of plant tissue age is reduced. However, the constancy of nutrient ratios and products is not without limits. Rates of change of concentrations of several nutrients may be quite rapid in very young plants and nutrient ratios and products may be correspondingly variable at this time. Nevertheless, these forms of expression are often less affected by aging processes and so present an opportunity to expand the usefulness and accuracy of foliar diagnosis. Essentially, the DRIS attempts to overcome the problems associated with plant age, nutrient interactions, and foliar optima determination (Walworth and Sumner, 1987, 1988).

In summary, the DRIS integrates nutrient concentration with nutrient balance for multiple nutrients to optimize accuracy of plant tissue analysis. Each of the 13 mineral nutrient ratios has two forms, e.g., N/P and P/N. In addition, DM ratios developed from tissue analysis are utilized to calculate ratios for the non-mineral atmospheric elements Carbon (CO₂), Oxygen (O₂), and Hydrogen (H₂O) (Walworth and Sumner, 1987, 1988). Traditionally, the ratio that results in the most significant variance ratio between the low- and high-yielding is selected to be used in calculations (Beaufils, 1957). This procedure is intended to determine the norms with the greatest predictive performance. Similar to resin capsules, the DRIS technology has been scientifically validated for enhancing foliar/plant tissue analysis, particularly via integration with soil analysis to provide precision delivery of nutrients and diagnosing both nutritional and non-nutritional problems (Walworth and Sumner, 1987, 1988).

The increase in crop yields and subsequent decrease in fertilizer applications resulting from improving soil and plant testing will eventually make integrated nutrient management software economically attractive to producers. The soil test will provide an accurate forecast of lime and fertilizer needs. Tissue and sap analysis will provide a clear picture of plant nutrients, which will identify nutritional disorders, evaluate fertilizer efficiency and reveal unknown relationships among essential elements. Plant analysis also reveals the effect of lime on the availability of native and applied elements. Accurate plant and algae tissue and sap analysis can be utilized to alert producers to the following:

- Plant phosphorus absorption: Not all soil phosphorus is available to plants. The only way to accurately determine if plant needs are met is with a whole plant tissue analysis.
- Nitrogen requirements: For many crops, nitrogen is the most expensive, out-of-pocket cost and also is the most critical nutrient for maximizing yields. Nitrogen recommendations are based on a number of factors; however, the best way to fine tune crop requirements is with plant tissue analyses.
- Secondary nutrient and micro-nutrient deficiencies: Soil tests can provide good information on these nutrients, but the gold standard for soil status is plant tissue and sap analyses.

- Very high or toxic levels of micro-nutrients: This is critical on land where municipal sewage is spread but can be an issue on all soils.
- Nutrient balance in the soil: Plant tissue analysis reports provide a unique graphic that highlights nutrients that are deficient, in the proper range and those that are high.

Relatively large data sets are now needed to correlate data with conventional sampling and chemical extraction technologies for soil and plant analyses for development of practical applications to improve NUE. Nutrient manager software also needs development for specific types of irrigation technologies and crop management with emphasis on precision agricultural applications. Conventional soil testing and resin capsule protocols have been developed for all lab processes in order to ensure uniform test results and accurate correlations.

Microbial Electrolysis Cell (MEC) Technology

Integration of precision agriculture and CEA with plant microbial fuel cells (MFCs) and/or microbial electrolysis cells (MECs) allows for simultaneous production of biogas and plant biomass. Microbial electrolysis is the process of producing electricity or biogas by the addition of a relatively small amount of electrical voltage similar to that required for a microbial fuel cell. The principal concept for aquatic plant MECs is based on the fact that plants exude organic matter, mostly in the form of carbohydrates, into the phytosphere. The phytosphere is the area immediately surrounding the roots or cells of the plant. Bacteria (electrogenic microbes) subsequently convert these organic nutrients into bioelectricity via plant MFCs, or biogases (CH₄ and H₂) via plant MECs. A considerable amount of fixed carbon is used for plant growth but a portion of it, which can range from 30-40% for young plants is exudated through the roots and microalgae membranes as phytodeposits/rhizodeposits (Badri and Vivanco, 2009; Whipps 1990; [Bais et al., 2006](#)). These organic molecules are then used as fuel and oxidized back to CO₂ at the microbial anode of an MFC/MEC application. Plant MECs provide opportunities for converting plant exudates such as organic acids, carbon-containing primary and secondary metabolites, and even CO₂ to CH₄.

MFC & MEC technologies are based on fermentative and electrolytic production of biogas and bioelectricity by microbial organisms. Fermentative hydrogen production involves dark fermentation, followed by biogas refining. Research reveals that two-step processes utilizing both dark fermentation and photo-fermentation yield the highest levels of hydrogen.

Fermentative hydrogen production is the conversion of organic substrates to biohydrogen manifested by a diverse group of exoelectrogenic bacteria using multi-enzyme systems. This anaerobic respiration process involves three microbial steps similar to anaerobic digestion. Dark fermentation reactions do not require light energy, so they are capable of constantly producing hydrogen from organic compounds throughout the day and night. Dark fermentation occurs either by mixed cultures of hydrogen producing sludge or pure cultures of anaerobic bacteria such as *Clostridium butyricum* and *Enterobacter cloacae*. Photo-fermentation is provided by bacteria such as the *Rhodobacter sphaeroides* (strain O.U.001) in a column photo-bioreactor. This integrated approach achieves higher yields of hydrogen by complete utilization of the chemical energy stored in the substrate ([Nath et al., 2005](#)).

Hydrogen production efficiency for dark fermentation is generally less than 15% due to thermodynamic limitations. Therefore, new technologies are required to optimize the use of organic matter, particularly organic constituents contained in wastewater, as a renewable resource. Unlike dark fermentation, biocatalyzed (microbial) electrolysis (MEC) is able to overcome thermodynamic limitations by means of a small input of electrical energy. MECs require less than 1.0 kWh/Nm³ H₂ compared with water electrolysis which requires more than 4.5 kWh/Nm³ H₂. For example, acetic acid, which is commonly found in thin stillage (which is a coproduct of bacterial infections derived from conventional ethanol biorefineries) converts very efficiently to hydrogen and carbon dioxide according to stoichiometry:



After successfully demonstrating the proof of principle for biocatalyzed electrolysis in 2004, ongoing research has focused on improving this MEC technology in order to develop a mature technology capable of producing over 10 Nm³ H₂/m³ of reactor volume/day at an applied voltage of about 0.3-0.4 Volt. The term “Nm³” refers to normal atmospheric conditions, i.e. ambient temperature and pressure per cubic meter (m³) of hydrogen biogas produced per m³ of substrate utilized.

Microbial Electrolysis Cell (MEC)

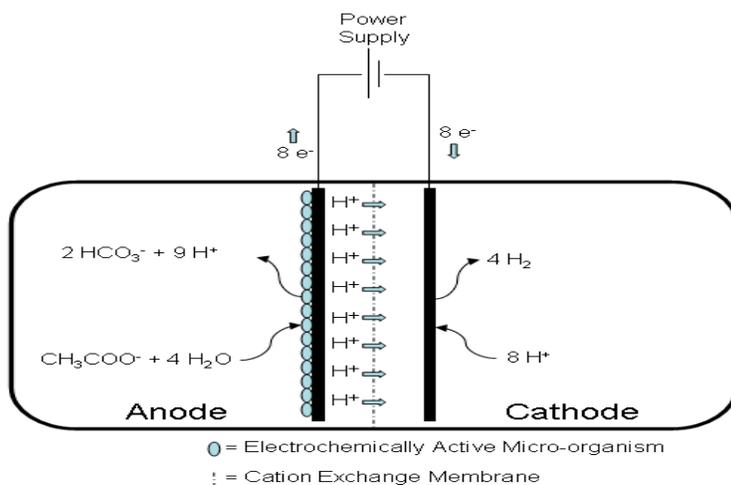


Figure 2. MEC with Cathode Exchange Membrane (Rozendal, 2004)

Several scientists have been developing a new hydrogen production process based on previous knowledge from MFC research. Like the MFC, biocatalyzed electrolysis utilizes electrochemically active microbes which provide hydrogen production efficiencies over 90%. This is possible due to improved MEC design and an understanding of the hydrogen evolution reaction (HER), i.e. the idea that protons and electrons produced by bacteria can be recombined at the cathode as hydrogen gas (H₂). Furthermore, the innovative design of the reactor allows for utilizing a much wider variety of substrates which are suitable for hydrogen production. This makes biocatalyzed electrolysis (MEC) a revolutionary breakthrough technology in the field of biological hydrogen production from organic waste, wastewaters, and cellulosic biomass (Rozendal, 2004).

In 2007, the efficiency of this revolutionary microbial electrolysis process was dramatically improved and renamed electrohydrogenesis by Bruce Logan's group at Penn State University. "At an applied voltage of 0.6 Volts, the overall energy efficiency of the process was 288% based solely on electricity applied (and 82% when the heat of combustion of acetic acid was included in the energy balance) at a gas production rate of 1.1 Nm³ of H₂ per m³ of reactor volume per day. This exothermic reaction can be utilized to regulate water temperature for CEA applications. In addition, the electrical current produced can be utilized to operate state-of-the-art light emitting diodes (LEDs) which are extremely energy efficient, thus reducing energy costs for integration of CEA and MEC technologies. Direct high-yield hydrogen gas production was further demonstrated by using glucose, several volatile acids (acetic, butyric, lactic, propionic, and valeric), and cellulose at maximum stoichiometric yields of 54–91% and overall energy efficiencies of 64–82%. The hydrogen gas produced was over 99.5% H₂ ([Cheng and Logan, 2007b](#))." In 2008, the cathode exchange membrane was eliminated for a single chamber MEC ([Call and Logan, 2008](#)), allowing for simplifying design and further reduction of production costs for commercial applications.

Further improvements to MEC design along with optimizing microbial environments by regulating temperature, pH, electrical conductivity (EC) and nutrient composition of substrates should continually reduce HRT. Currently, MECs appear to be capable of processing organic wastewater in about 11 hours. This is substantially more efficient than high rate anaerobic digestion which requires 4-10 days using state-of-the-art technology. Though MEC technology is not expected to replace high rate anaerobic digestion, the potential synergies for using anaerobic digester effluents to enhance production of functional foods and biomass via integration of CEA and MEC applications is very encouraging.

Utilizing the biological effluent (which remains after hydrogen extraction) as a value added fertigation stream maximizes overall production efficiency via integration of closed loop biomass and food production systems. Next generation algal bioreactors will produce lignin-free cellulosic biomass containing between 30-75% lipids for synthetic algae. Algal bioreactors are predicted to produce from 10,000 to 100,000 gallons of biodiesel per acre depending on efficiency of photobioreactor design. In addition, ethanol, protein rich animal feedstuffs, nutraceuticals, biochemicals, and bioplastics can be produced from the remaining algal biomass. The value of the functional foods, nutraceuticals/pharmaceuticals, industrial biochemicals, biofuels and animal feedstuffs produced from lignocellulosic and algal biomass via biological effluents is expected to exceed the value of biohydrogen and bioelectricity produced by MECs and MFC configurations. Plant MFC/MEC technologies do not inhibit production of plant biomass.

Stainless Steel Brush Cathodes for MECs

"Microbial electrolysis cells (MECs) are an efficient technology for generating hydrogen gas from organic matter, but alternatives to precious metals are needed for cathode catalysts. High surface area stainless steel (SS) brush cathodes have been developed which produce hydrogen at rates and efficiencies similar to those achieved with platinum-catalyzed carbon cloth cathodes in single-chamber MECs. Using a stainless steel brush cathode with a specific surface area of 810 m²/m³, hydrogen was produced at a rate of 1.7 +/- 0.1 m³-H₂/m³-d (current density of 188 +/- 10

A/m³) at an applied voltage of 0.6 V. The energy efficiency relative to the electrical energy input was 221 +/- 8%, and the overall energy efficiency was 78 +/- 5% based on both electrical energy and substrate utilization. These values compare well to previous results obtained using platinum on flat carbon cathodes in a similar system. Reducing the cathode surface area by 75% decreased performance from 91 +/- 3 A/m³ to 78 +/- 4 A/m³. A brush cathode with graphite instead of stainless steel and a specific surface area of 4600 m²/m³ generated substantially less current (1.7 (0.0 A/m³), and a flat stainless steel cathode (25 m²/m³) produced 64 (1 A/m³, demonstrated that both the stainless steel and the large surface area contributed to high current densities. Linear sweep voltammetry revealed that the stainless steel brush cathodes reduced the overpotential needed for hydrogen evolution and exhibited a decrease in over-potential over time as a result of activation. These results demonstrate for the first time that hydrogen production can be achieved at rates comparable to those with precious metal catalysts in MECs without the need for expensive cathodes.

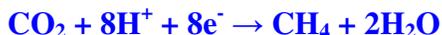
Using high surface area SS brushes as cathodes in MECs is an important step toward building larger scale reactors that are economical because it avoids the use of expensive catalysts. Platinum currently costs ~\$43,000/kg compared to \$4.82/kg for 304 grade SS ([Kitco](#) and [MEPS](#)), which translates into a cost of \$0.03 for the half SS brush cathode and \$0.15 for the Pt or the Pt/C cathode used in this study (excluding the cost for the carbon cloth, Nafion binder, and current collector). [Rozendal et al. \(2008\)](#) and [Liu et al. \(2008\)](#) determined that the cathode (including catalyst) accounts for the greatest percentage (47%) of the total capital costs for both MFCs and MECs. Their models predict that cathodes will play a smaller role in the total reactor cost by identifying materials that have substantially lower costs than those currently used. Clearly, the use of SS instead of Pt moves cathode designs closer to that goal.” ([Call et al., 2009](#))

Potential for Efficient & Economical Electromethanogenesis via Plant MECs

In addition to producing hydrogen, methane can be directly produced using a biocathode containing methanogens in electrochemical systems (abiotic anode) or microbial electrolysis cells (MECs; biotic anode) by a process called electromethanogenesis. At a set potential of less than -0.7 V (vs Ag/AgCl), carbon dioxide was reduced to methane using a two-chamber electrochemical reactor containing an abiotic anode (biocathode), and no precious metal catalysts. At -1.0 V, the current capture efficiency was 96%. Electrochemical measurements made using linear sweep voltammetry showed that the biocathode substantially increased current densities compared to a plain carbon cathode where only small amounts of hydrogen gas could be produced. Both the biocathode and the carbon cathode increased current densities and very small hydrogen production rates by a plain cathode, thereby supporting a mechanism of methane production directly from current and not from hydrogen gas.

The biocathode was dominated by a single Archaeon, *Methanobacterium palustre*. When a current was generated by an exoelectrogenic biofilm on the anode growing on acetate in a single-chamber MEC, methane was produced at an overall energy efficiency of 80% (electrical energy and substrate heat of combustion). These results reveal that electromethanogenesis can be used to convert electrical current produced from renewable energy sources (such as wind, solar, or biomass) into a biofuel (methane) as well as serving as a method for the capture of CO₂. Researchers discovered that Archaea, using about the same electrical input for processing of

acetic acid, could use the current to convert CO₂ and water to methane without any organic material, bacteria or hydrogen usually found in MECs.



The advantage of utilizing electromethanogenesis in comparison with electrohydrogenesis is that methane is more readily used in today's economy than hydrogen, except for production of ammonia. The technological advantage of using biomethane is due to leveraging current natural gas infrastructures and high temperature fuel cells which are designed to run on methane-rich feeds for production of bioelectricity. In this example, biomethane is utilized as a hydrogen-rich energy carrier, e.g. a renewable fuel for distributed generation of combined heat and power and cogeneration of biohydrogen (DG-CHP & H₂). For closed loop systems total energy efficiency can approach 90% for integrated biorefineries via a carbon neutral process. A portion of the power, CO₂ and waste heat produced by the high temperature fuel cell is utilized to provide electrical current, space heat and nutrients for integration of plant MECs and CEA for aquatic plant species such as algae and water hyacinth.

As alluded to above, transforming electrons into methane has the advantage of producing a hydrogen-rich fuel that can easily be stored or transported in comparison with pure hydrogen. Compression technology, transporting in pipes, and storage of methane involves mature technologies, and thus methane production by electromethanogenesis could immediately be integrated into existing energy infrastructures. Similarly, ammonia synthesized from hydrogen and inert N₂ in the atmosphere via the Harber-Bosch process can also be transported through existing pipeline and distribution infrastructures. The efficiency of CO₂ capture demonstrated by electromethanogenesis is high in comparison to other methods and thus may be useful for recycling carbon. As listed above, electrochemical reduction of CO₂ using electromethanogenesis has an electron capture efficiency of 96%, compared to 10-57% using metal catalyzed electrodes for methane production (Jitaru, 2007).

The use of Archaea bacteria for producing methane via electromethanogenesis provides an additional route for biofuel production accompanied with CO₂ capture, without the need for precious metal catalysts. The use of a methanogenic biocathode enables methane production from any electrical source, although renewable energy sources including fuel cells running on biomethane produced from biogas or direct solar energy would provide the greatest advantages for sustainable bioenergy systems.

Municipal BioEnergy Complex
Closed Loop Modular DG-CHP On-Demand

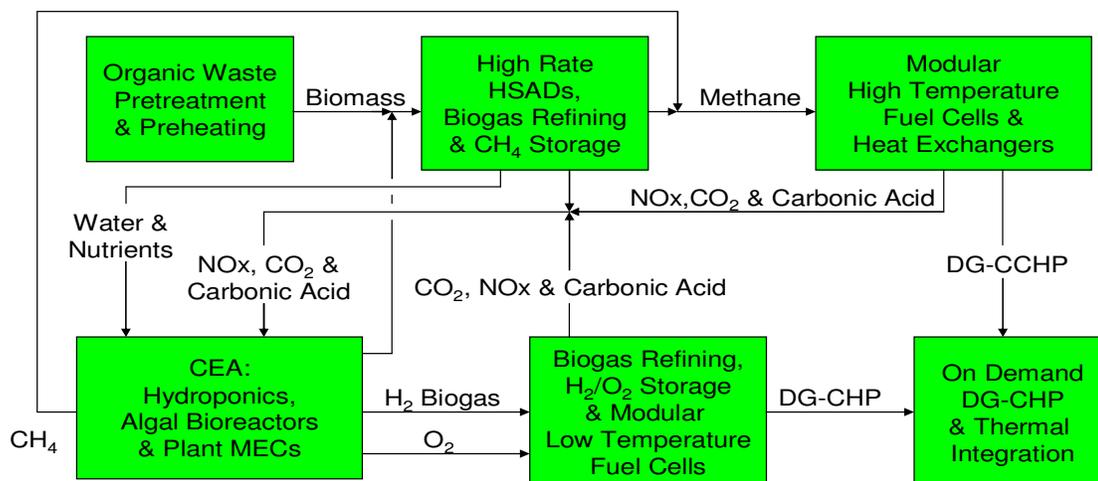


Figure 3. Integration of Organic Waste Processing, CEA & Plant MECs.

The production of methane by electromethanogenesis will likely not displace existing methods of biomethane production from organic matter using anaerobic digesters, especially for wastewaters with large volumes of raw organic matter. MECs will likely be more appropriate for treatment of relatively dilute wastewaters such as nutrient-rich biological effluents utilized as value added fertigation streams for integration of MECs with CEA. The above research project reveals that microorganisms can be used in the form of biofilm on the cathode of an MEC to produce methane gas from electrical current at rates much greater than those possible via hydrogen gas evolution from a noncatalyzed electrode ([Cheng et al., 2009](#)).

The opportunity to simultaneously produce biomethane and biohydrogen via MECs in addition to third generation biomass feedstocks such as algae and water hyacinth would substantially increase sustainability of the biofuels industry, particularly for integrated biorefineries and bioenergy complexes. If next generation algal bioreactors and hydroponic greenhouses are designed to accommodate plant MECs, methane and/or hydrogen biogas could be produced in addition to biofuels and bioelectricity via integrated biorefineries and bioenergy complexes which incorporate closed loop architecture.

In summary, through photosynthesis by micro-organisms (algae) as well as by higher plants, solar energy is converted to chemical energy stored in biomass or carbon rich chemical compounds. Mixed microbial communities provide the possibility to exploit this chemical energy by converting it to useful energy (carriers) such as biogas and bioelectricity.

MFC/MEC Technology & Comprehensive Nutrient-Energy Management

MFCs function efficiently under mild conditions relative to other types of fuel cells. Operating temperatures range from 20-40 °C. However, optimal yields of biogas and biopower are achieved between 35-40 °C (mesophilic) with the capability of producing over 80% total energy efficiency. With thermal integration for controlled environment applications, total energy efficiency could exceed 90%. This is two to three fold more energy than conventional internal combustion engine (ICE) and turbine engine technologies are capable of producing. Essentially, MFCs & MECs produce about two to three times more energy than they consume. MFCs are

suitable for small scale applications such as potential medical devices fueled by glucose contained in blood, or larger applications such as wastewater treatment plants, ethanol biorefineries, and breweries which produce organic waste that can be used as nutrient-energy rich substrates which serves as electrolytes for MFCs.

The electrolyte utilized in an MFC is water containing free ions that behave as an electrically conductive medium. Hence, optimizing electrical conductivity by regulating salinity of the electrolyte is crucial. Because electrolytes generally consist of ions in solution, particularly for use in batteries and fuel cells, electrolytes are also known as ionic solutions. Electrons complete the circuit by traveling to the cathode, where they are taken up by oxygen and hydrogen ions to form water. Thus, the air cathode utilizes oxygen to produce water while the anode biofilm oxidizes organic matter in an anaerobic environment which optimizes power production (Coulombic efficiency) and produces CO₂ at the anode. The water that is produced at the air-cathode can be mixed with essential plant nutrients which remain after processing organic matter comprising nutrient-rich biological effluents. These biological effluents may be processed into value added fertigation streams, which along with capturing carbon dioxide emissions as a value added fertilizer, may be utilized for closed loop production systems for functional foods and biomass energy crops.

Advantages of MFC & MEC BioEnergy Technologies

- Biocatalysts (communities of microbial organisms capable of either exocellular or extracellular electron transfer) provide for efficiently converting organic matter (particularly abundant sources of organic waste substrates contained in wastewaters) into bioelectricity, biohydrogen, and biomethane.
- Bioelectricity is produced directly from organic waste, crop residues, biorefinery wastewater, and other forms of lignocellulosic biomass contained in domestic and industrial wastewaters ([Cheng and Logan, 2007b](#); [Huang and Logan, 2008a](#); [Huang and Logan, 2008b](#); [Rezaei et al., 2008](#)). This is in contrast to conventional aeration processes which actually consume 1.5% of current power generation.
- MFC & MEC technologies can be used to process an abundant supply of organic waste from CAFOs, food processing, and municipal wastewaters while simultaneously reducing pollutants via using value added fertigation streams and carbon dioxide for production of food & bioenergy via closed loop systems.
- Operating at ambient or mesophilic temperatures, it is possible to increase total energy efficiency (production of biopower, biomethane and biohydrogen) by two to three fold in comparison with internal combustion and turbine engines while eliminating emissions. H₂ is produced from electrons (current) via exoelectrogenic bacteria while CH₄ is typically produced by methanogenic bacteria from acetate and other organic compounds. However, methane has recently been produced by electromethanogenic bacteria via MECs in a process called electromethanogenesis without requiring precious metal cathodes ([Cheng et al., 2009](#)).
- Hydraulic retention time (HRT) for organic waste processing via MFC is estimated to be about 11 hours ([Liu et al., 2008](#)) in comparison with 4-16 days for high rate anaerobic digestion (AD), and 16-30 days for conventional AD. HRT for MFCs depends on loading rate and amount of electrode surface area per volume.
- Odors from animal waste can be reduced by over 99% via MFCs ([Kim et al., 2008b](#)).

- Integration of MFC/MEC and high temperature MCFC or SOFC technologies can be utilized to provide thermal integration for mesophilic MFC/MEC applications via DG-CHP for bioenergy complexes; and coproduction of biohydrogen, biomethane, and biohythane. Using biomethane as a feed, the MCFC can also provide coproduction of biohydrogen (via PEM technology) from either biomethane or biogas.
- MEC applications produce a biogas consisting of either 99.5% hydrogen gas (trace amounts of CO₂ and CH₄) or 99.5% methane for use in fuel cells. This eliminates the need for removing H₂S and siloxane from MEC biogas for use in high temperature fuel cells.
- Similar to engineering microbes for improving production of ethanologens, microbial engineering could eventually enhance efficiency of MFC and MEC applications via engineering of exoelectrogens, i.e. microbes which are capable of exocellular electron transfer ([Xing et al., 2008](#); [Zuo et al., 2008a](#); [Ren et al., 2007](#)). (Exocellular refers to electron transfers that are initiated inside a cell but actually take place outside the cell, such as anaerobic respiration by both bacteria and yeast.)
- For thermally integrated operations, such as bioenergy complexes, in temperate climates MFCs & MECs could be co-located in insulated buildings along with CEA, AD, and MCFC applications. This would eliminate transportation costs and allow for thermally regulating mesophilic MFCs and MECs using waste heat recovery from high temperature fuel cells and other integrated biorefinery operations.
- The heat generated from MECs along with latent heat provided by high temperature MCFCs integrated with CEA such as hydroponic greenhouses could essentially eliminate the need for additional energy inputs for year round biomass production in temperate climates.

Systems Architecture

Optimizing nutrient-energy management for integrated operations such as bioenergy complexes will require balancing the volume of organic waste processing via AD & high temperature fuel cells which provide CHP & biohydrogen production, with MFC/MEC applications which produce biopower, biomethane, and biohydrogen. Theoretically, all of these fuel cell technologies can achieve over 90% total energy efficiency via thermal integration and incorporation of closed loop production systems. The 11 hour HRT for MFC/MEC applications and lack of having to remove contaminants from biogas are strong economic advantages over AD & high temperature fuel cell technologies. However, mesophilic MFC/MEC applications require energy in the form of heat to reach maximum efficiency for biopower production. High temperature fuel cells can provide thermal integration via DG-CHP configurations which efficiently recover waste heat. Carbonic acid produced from condensation during heat recovery processes, space heat and carbon dioxide from MCFC exhaust can be utilized for enhancing biomass production via CEA applications such as algal bioreactors.

Thermal Integration & Comprehensive Nutrient-Energy Management Enclosed Insulated Structure for Temperate Climates

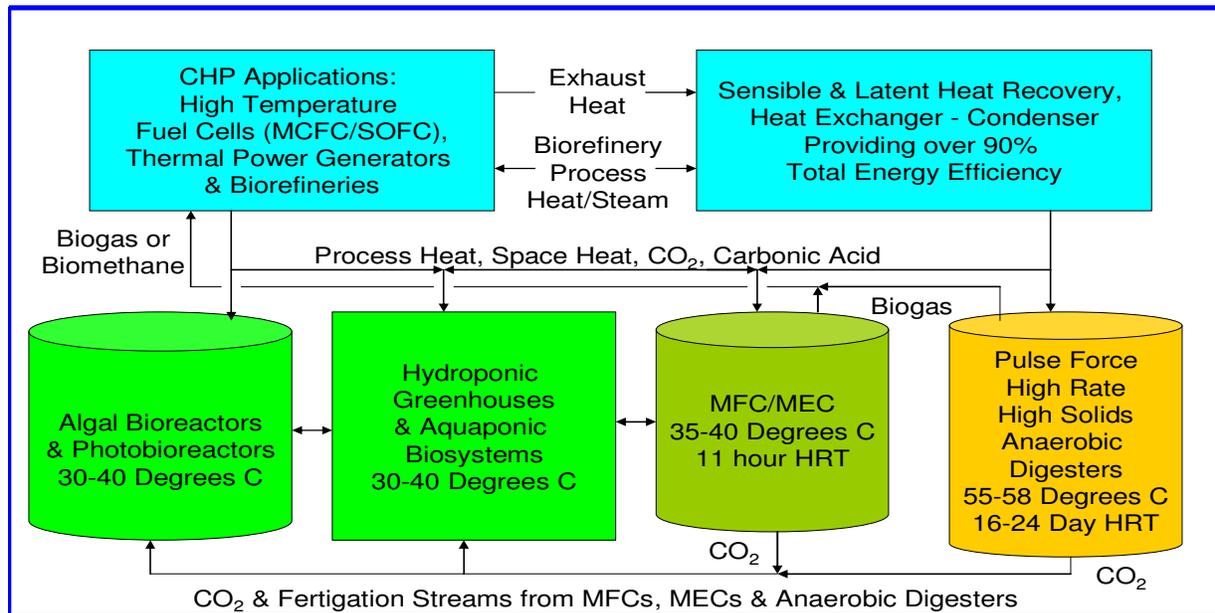


Figure 4. Achieving over 90% total energy efficiency via thermal integration.

The quality of the biological effluents from MFC & MEC applications, which can possibly be used as value added fertigation streams for closed loop production, are critical economic factors which need to be determined for bioenergy complexes. Based on \$6/bu corn and biological effluents produced by conventional anaerobic digester systems, the quantity of the biomass that can be produced is worth about 10-12 times the value of the biomethane which is extracted from organic waste. Since MFC/MECs efficiently utilize organic acids contained in thin stillage and brewery wastewater (Feng et al., 2008; Hawkes et al., 2007; Min and Logan, 2004; Logan, 2004), that could be the most efficient application for integration with ethanol biorefineries and breweries. In addition to providing thermal integration for mesophilic MFC/MECs, high temperature fuel cells could efficiently provide low levels of power required for MEC applications via closed loop production systems.

There are a variety of organic substrates and municipal/industrial waste streams which can be utilized as feeds for MFCs. For example, thin stillage and brewery wastewater which remains after microbial (primarily yeast) fermentation processes produce ethanol, is relatively rich in COD/BOD, contains organic acids which are optimal feeds for MFCs, and is preheated for optimizing power production via integration of MFCs.

The scientific breakthrough leading to development of MFC/MEC technologies is translated into applied biotechnology by using modern membrane and electrode materials that are compatible with biofilm growth and operation at ambient or near ambient (mesophilic) temperatures. This is accomplished via thermal integration at integrated operations which maximizes production of bioenergy. Optimizing density of the biofilm at the anode increases electron transfer to the anode which maximizes power generation (Microbial Fuel Cell Organization, 2008; Biodesign Institute, Arizona State University, 2008; Marcus & Rittman, 2008).

Anaerobic Digestion

Organic waste resources (such as biorefinery wash water and thin stillage, food processing waste, animal waste, and municipal wastewater) contain only 2-13% solids. Though these high moisture organic wastes are not efficient for processing by energy intensive gasification or pyrolysis technologies, they are ideal for anaerobic digestion which occurs near ambient temperatures via biochemical conversion processes.

Anaerobic digestion relies on microorganisms (microbes) to transform organic waste into biogas. Anaerobic digesters which process waste under oxygen-free conditions are different than conventional aerobic systems that use oxygen to treat organic waste. “Anaerobic digesters can process five to ten times more organic waste than aerobic systems. Because the waste is enclosed to keep oxygen out, anaerobic digestion reduces odorous emissions. Flies, other insects and pathogens are also reduced by as much as 95%. With anaerobic digestion, the methane produced can be used to produce combined cooling, heat and electrical power generation, and hydrogen cogeneration, thus eliminating greenhouse gas emissions (GHGEs) that contribute to global warming. Nutrients such as nitrogen and phosphorus can be recovered and used to fertilize crops. The by-products of anaerobic digestion -- liquid fertilizer and compost -- reduce the need for synthetic fertilizers and soil conditioners that are produced using less sustainable methods, providing a cost savings as well as environmental benefits.” ([Wilkie, 2007](#))

Anaerobic digestion reduces the potential for global warming in two ways:

- by capturing biogas, it can reduce natural methane GHGE
- when it produces renewable biomethane to replace fossil fuels such as coal, oil and natural gas, production of carbon dioxide from burning those fossil fuels is avoided

Another advantage of anaerobic digestion is that it produces relatively low volumes of sludge which require further processing and disposal. In fact the sludge serves as a valuable organic fertilizer. This is in direct contrast to aerobic processing which produces large volumes of sludge. ([Wilkie, 2006](#))

Anaerobic digestion is a holistic manure and organic waste treatment system which not only stabilizes organic waste, it produces energy, controls odors, reduces pathogens, minimizes environmental impact from waste emissions, and maximizes fertilizer and water recovery for reuse in comprehensive nutrient-energy management and innovative crop producing systems for integrated operations. For example, closed loop biomass can be produced year round using waste heat and organic waste streams for controlled environment agriculture such as algal bioreactors and hydroponic greenhouses, providing unprecedented production efficiencies for both food and bioenergy feedstocks.

In recent years, increasing awareness that anaerobic digesters can help control the disposal and odor of animal waste has stimulated renewed interest in the technology. Dairy farmers faced with increasing Federal and State regulation of the waste their animals produce are looking for ways to comply. New digesters now are being built because they effectively eliminate the environmental hazards of dairy farms and other confined animal feeding operations (CAFOs).

With the Clean Water act of 1977 and the final rule for CAFO's in 2003, confined animal feeding operations have become a point source of pollution in contrast to agriculture in general

which has traditionally been classified as a non-point source. EPA regulations for CAFO's state that polluting ground water or surface water with manure and/or nutrients is illegal. Fines for CAFO pollution are administered by the EPA in partnership with individual states. In addition, the Clean Air Act of 1990 is resulting in new regulations for CAFOs to control odors and reduce methane emissions. Similar nutrient management issues for organic waste also pertain to food processing and municipal waste management.

According to the EPA, "methane (CH₄) is emitted from a variety of both human-related (anthropogenic) and natural sources. Human-related activities include fossil fuel production, animal husbandry (enteric fermentation in livestock and manure management), rice cultivation, biomass burning, and waste management. These activities release significant quantities of methane to the atmosphere. It is estimated that more than 60% of global methane emissions are related to human activities ([IPCC, 2007](#)). Natural sources of methane include wetlands, gas hydrates, permafrost, termites, oceans, freshwater bodies, non-wetland soils, and other sources such as wildfires.

Methane emission levels from a source can vary significantly from one country or region to another, depending on many factors such as climate, industrial and agricultural production characteristics, energy types and usage, and waste management practices. For example, temperature and moisture have a significant effect on the anaerobic digestion process which is one of the key biological processes that cause methane emissions in both human-related and natural sources. Also, the implementation of technologies to capture and utilize methane from sources such as landfills, coal mines, and manure management systems affects the emission levels from these sources.

Emission inventories are prepared to determine methane contribution from different resources. The following sections present information from inventories of US man-made sources and natural sources of methane globally.

Human-related Sources of Methane

In the United States, the largest methane emissions come from the decomposition of wastes in landfills, ruminant digestion and manure management associated with domestic livestock, natural gas and oil systems, and coal mining.

The following table lists the level of emissions from individual sources for the years 1990, 1995, 2000 and 2005 to 2007. Those sources of methane emissions which can be either directly or indirectly affected via efficient production of livestock and improving efficiency for waste management are highlighted in blue. These sources currently represent 84% of methane emissions in the US.

Efficient waste management using anaerobic digestion provides an opportunity for capturing the majority of methane emissions and using them as a renewable biofuel. Biomethane can displace natural gas consumption for both residential and commercial applications. For example, biomethane can be utilized as a feed for high temperature fuel cells which provide DG-CHP and coproduction of hydrogen. Integrated operations can essentially eliminate carbon dioxide and

nitrous oxide emissions free via closed loop systems architecture which allows for producing biomass via CO₂ enrichment and the potential for achieving 90% total energy efficiency.

Table 4. U.S. Methane Emissions by Source (TgCO₂ Equivalents)

Source Category	1990	1995	2000	2005	2006	2007
Enteric Fermentation (cattle)	133.2	143.6	134.4	136.0	138.2	139.0
Landfills	149.2	144.3	122.3	127.8	130.4	132.9
Natural Gas Systems	129.6	132.6	130.8	106.3	104.8	104.7
Coal Mining	84.1	67.1	60.5	57.1	58.4	57.6
Manure Management	30.4	34.5	37.9	41.8	41.9	44.0
Forest Land Remaining Forest Land	4.6	6.1	20.6	14.2	31.3	29.0
Petroleum Systems	33.9	32.0	30.3	28.3	28.3	28.8
Wastewater Treatment	23.5	24.8	25.2	24.3	24.5	24.4
Stationary Combustion	7.4	7.1	6.6	6.7	6.3	6.6
Rice Cultivation	7.1	7.6	7.5	6.8	5.9	6.2
Abandoned Underground Coal Mines	6.0	8.2	7.4	5.6	5.5	5.7
Mobile Combustion	4.7	4.3	3.4	2.5	2.4	2.3
Composting	0.3	0.7	1.3	1.6	1.6	1.7
Petrochemical Production	0.9	1.1	1.2	1.1	1.0	1.0
Field Burning of Agricultural Residue	0.7	0.7	0.8	0.9	0.8	0.9
Iron and Steel Production & Metallurgical Coke Production	1.0	1.0	0.9	0.7	0.7	0.7
Ferroalloy Production	+	+	+	+	+	+
Silicon Carbide Production and Consumption	+	+	+	+	+	+
International Bunker Fuels	0.2	0.1	0.1	0.1	0.1	0.1
Total for U.S.	616.6	615.8	591.1	561.7	582.0	585.3

Sources: [U.S. Emissions Inventory 2009: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2007](#)

According to the above inventory, the total amount of methane which could be annually produced from organic waste and recycled as a renewable biofuel is 481 TgCO₂. This is

equivalent to 21 million metric tonnes of CH₄, e.g. 110 trillion BTUs. This represents about 10% of the entire volume of methane annually consumed in the US. Anaerobic processing of municipal sewage based on production via 0.20 AU *per capita* could potentially increase biomethane production to almost 20% of US consumption.

Livestock Enteric Fermentation

Among domesticated livestock, ruminant animals (cattle, buffalo, sheep, goats, and camels) produce significant amounts of methane as part of their normal digestive processes. In the rumen, or large fore-stomach, of these animals, microbial fermentation converts feed into products that can be digested and utilized by the animal. This microbial fermentation process, referred to as enteric fermentation, produces methane as a by-product, which can be exhaled by the animal. Methane is also produced in smaller quantities by the digestive processes of other animals, including humans, but emissions from these sources are insignificant. The [U.S. inventory report](#) provides a detailed description on methane emissions from livestock enteric fermentation and how they are estimated (see the Chapter entitled "Agriculture").

Globally, livestock are the largest source of methane from human-related activities – and in the US, the third largest source. Livestock production can also result in emissions of nitrous oxide, a very potent greenhouse gas, and carbon dioxide, the most abundant greenhouse gas. Fortunately, there are ways to reduce greenhouse gas emissions from livestock production through management strategies that improve production efficiency and result in lower emissions per unit of milk or meat produced.

Emissions studies reveal that one of the most effective strategies for reducing VOCs and GHGE is simply improving livestock production efficiencies in which emissions are reduced simultaneously. Beginning with diet formulations, improving nutrient content in rations can increase feed efficiency of animals by 20-40% according to feed trials (Kerely, 2007). For ruminants this is accomplished by optimizing protein and amino acid requirements of both microbial bacteria and the animal. Rumen degradable protein (McCarthy et al., 1989; Rooke and Armstrong, 1989; Cecava et al., 1990) and rumen undegradable protein (Titgemeyer et al., 1989; Cecava and Parker, 1993; Coomer et al., 1993) have been examined for their effects on animal performance and synthesis of microbial crude protein associated with microbial efficiency. In recent years much attention has focused on the amino acid requirements of the animal (Ludden and Cecava, 1995). Researchers have become more knowledgeable regarding specific amino acid requirements and providing those in the proper balance has resulted in more efficient feed:gain ratios (Cecava and Parker, 1993).

Beef cattle in feedlots are routinely fed rations which contain excessive amounts of protein while dairy cattle are often fed excessive amounts of fat. While excessive protein results in increasing enteric methane emissions, ammonia emissions and urea hydrolysis, excessive fat results in manure with excessive phosphorus levels. Both nitrogen and phosphorus are major components of nutrient loading which contributes to nutrient loading, nutrient run-off, and subsequent pollution. Balancing livestock diets optimizes nutrient ratios in animal waste substrates utilized as feedstocks for anaerobic digesters. This subsequently reduces ammonia and H₂S emissions during anaerobic digestion. It also reduces the amount of processing required for converting anaerobic digester effluents into balanced fertilizers for optimizing plant growth. This is

particularly critical for closed loop production of food and energy crops. Protein-rich feedstuffs produced as distillers coproducts of biorefining provide low cost feedstuffs which are ideal for balancing livestock rations.

Livestock Waste Management

Methane is produced during the anaerobic (i.e., without oxygen) decomposition of organic matter in livestock manure management systems. Liquid manure management systems, such as lagoons and holding tanks, can cause significant methane production and these systems are commonly used at larger swine and dairy operations. Manure deposited on fields and pastures, or otherwise handled in a dry form, produces insignificant amounts of methane. However, land application of raw manure on crop fields contaminates food supplies and contributes substantially to nutrient loading and nutrient run-off. The [U.S. inventory report](#) provides a detailed description on methane emissions from livestock manure management and how they are estimated (see the Chapter entitled "Agriculture").

EPA has established a voluntary program to reduce methane emissions in the livestock industry. This program, known as the [AgSTAR Program](#), encourages adoption of anaerobic digestion technologies that recover and combust biogas (methane) for odor control or as an on-farm energy resource.

Landfills

Prior to being overtaken by livestock production in 2007, landfills were the largest human-related source of methane in the US, accounting for 34% of all methane emissions. Methane is generated in landfills and open dumps as waste decomposes under anaerobic conditions. The amount of methane created depends on the quantity and moisture content of the waste and the design and management practices at the site. The [U.S. inventory report](#) provides a detailed description on methane emissions from landfills and how they are estimated (see the Chapter entitled "Waste").

EPA has established a voluntary program to reduce methane emissions from landfills. This program, known as the [Landfill Methane Outreach Program](#) (LMOP), works with companies, utilities, and communities to encourage the use of landfill gas for energy. Much of the municipal solid waste including waste paper that is dumped at landfills could be economically processed into methane and organic fertilizers via anaerobic digestion.

Natural Gas & Petroleum Systems

Methane is the primary component of natural gas. Methane losses occur during the production, processing, storage, transmission, and distribution of natural gas. Because gas is often found in conjunction with oil, the production, refinement, transportation, and storage of crude oil is also a source of methane emissions. The [U.S. inventory report](#) provides a detailed description on methane emissions from natural gas and petroleum systems and how they are estimated (see the Chapter entitled "Energy").

EPA has established a voluntary program to reduce methane emissions in the natural gas industry. This program, known as the [Natural Gas STAR Program](#) (Gas STAR) is a voluntary

partnership between EPA and the natural gas and oil industries to reduce emissions of methane from the production, transmission, and distribution of natural gas.

Production of biogas and biomethane from organic waste resources can reduce US consumption by up to 20%, thus reducing emissions from reduced use and processing of natural gas.

Wastewater Treatment

Wastewater from domestic (municipal sewage) and industrial sources is treated to remove soluble organic matter, suspended solids, pathogenic organisms, and chemical contaminants. These treatment processes can produce methane emissions if organic constituents in the wastewater are treated anaerobically and if the methane produced is released to the atmosphere. In addition, the sludge produced from some treatment processes may be further biodegraded under anaerobic conditions, resulting in methane emissions.

These emissions can be avoided, however, by treating the wastewater and the associated sludge under aerobic conditions or by capturing methane released under anaerobic conditions. The [U.S. inventory report](#) provides a detailed description on methane emissions from wastewater treatment and how they are estimated (see the Chapter entitled "Waste").” ”([US EPA, Methane Sources and Emissions, 2009](#))

Ecological & Economical Factors which Promote Adoption of Anaerobic Digestion

Due to the growing number of clean water, clean air and soil regulations and fluctuation of commodity pricing for natural gas and electricity, it is often the environmental reasons and production of value added organic fertilizers - rather than the anaerobic digester's electrical and thermal energy generation potential - that motivates farmers, food processors, municipal wastewater facilities, and biorefineries to use anaerobic digester technology. This is especially true in areas where natural gas and electric power costs are relatively low. When utilized with integrated operations, unsurpassed efficiencies of operation can be achieved for anaerobic digestion of organic waste for CAFOs, food processing waste, biorefinery and industrial waste and municipal waste facilities.

Anaerobic digester systems, particularly thermophilic digesters, can reduce fecal coliform bacteria in animal waste and other forms of organic waste by more than 99%, virtually eliminating a major source of crop/food contamination and water pollution. Separation of the solids during the digester process removes about 25-60% of the nutrients from organic matter including animal and municipal waste, and the solids can be sold out of the drainage basin where nutrient loading may be a problem. After methane and CO₂ are produced via biogas, the digester effluent can be utilized as a nutrient rich liquid fertilizer. In many cases, the digester effluent can qualify as an organic fertilizer for use in organic or natural food production.

In addition, the digesters ability to produce and capture methane from the manure reduces the amount of methane that otherwise would enter the atmosphere. Scientists have targeted methane gas in the atmosphere as a contributor to global climate change. In terms of the greenhouse effect, methane is twenty three times more damaging to our environment than carbon dioxide.

During anaerobic digestion, several types of bacteria break down complex organic wastes in distinct stages. There are four basic types of microbes involved. Hydrolytic bacteria break down complex organic wastes into sugars and amino acids. Fermentative bacteria then convert those products into organic acids. Acidogenic microbes convert the acids into hydrogen, carbon dioxide and acetate. Finally, the methanogenic bacteria produce biogas from acetic acid, hydrogen and carbon dioxide.

Controlled anaerobic digestion requires an airtight chamber, often called a digester or reactor. To promote bacterial activity, the digester must maintain a temperature of at least 68 °F. Ambient temperature range is from 68 °F to 95 °F while mesophilic digesters range from 95 °F up to 104 °F. Using higher temperatures, up to 150 °F (the optimal range for thermophilic digesters is 135-150 °F) shortens processing time and reduces the required volume of the digester tank by 25% to 40%. There are more species of anaerobic bacteria that thrive in the temperature range of a standard design (mesophilic bacteria) than there are species that thrive at higher temperatures (thermophilic bacteria). High-temperature digesters also are more prone to upset because of temperature fluctuations and their successful operation requires close monitoring and diligent maintenance. Precautionary measures, such as insulated digesters and maintaining constant digester temperatures, optimal solids ratios and pH ranges can eliminate most of the concerns for efficient and reliable operation of thermophilic digesters.

The biogas produced in a digester is actually a mixture of gases, with methane and carbon dioxide comprising about 99% of the total. Biogas typically contains small amounts of hydrogen sulfide, nitrogen (in the form of ammonia gas), hydrogen, methylmercaptans and oxygen.

Methane is a combustible gas. The energy content of digester gas depends on the amount of methane it contains. Methane content varies from about 55% to 80%. Typical digester gas, with a methane concentration of 65%, contains about 650 BTU of energy per cubic foot. 80% methane contains 800 BTU of energy per cubic foot.

For individual farms, small-scale plug-flow or covered lagoon digester of simple design can produce biogas for on-site electricity and heat generation. For example, a plug-flow digester could process 8,000 gallons of manure per day, the amount produced by a herd of 500 dairy cows. By using digester gas to fuel an engine-generator, a digester of this size would produce more electricity and hot water than the dairy consumes.

Larger scale digesters are suitable for manure volumes of 25,000 to 100,000 gallons per day. In Denmark and in several other European countries, central digester facilities use manure and other organic wastes collected from individual farms and transported to the facility. However, handling and transportation of organic waste is time consuming and expensive. On-site digesters are considerably more efficient, particularly for large CAFOs, integrated biorefineries, and municipal wastewater treatment plants.

Anaerobic bacteria used in digesters are more efficient at processing fatty acids, carbohydrates and other VS than are many conventional yeast or algae strains using fermentation technologies. Most ethanologens are incapable of processing fatty acids into biofuels. Anaerobic digestion is

also about ten times more efficient than aerobic processing technologies. The efficiency of anaerobic digester technologies, which varies widely, is determined by:

- type of substrates digested
- use of particulate reduction and nutrient optimizing technology to enhance solids destruction and optimize microbial metabolism
- carbon:nitrogen ratio
- loading rate (percent solids)
- hydraulic retention time (HRT) which ranges from 4 days to 60 days
- operating temperature (mesophilic or thermophilic) which determines destruction of pathogens
- methane concentration of biogas which ranges from 50%-80%
- cost of operating and maintaining the digester as a percent of total gross energy produced (this ranges from 10% to 35%)

Anaerobic Digestion & Comprehensive Nutrient-Energy Management

From an ecological standpoint, similar BTU values for raw biomass and animal manure indicate that maximum energy efficiency is achieved by first processing biomass as biofuel feedstocks. However, animal waste is often limiting in nitrogen content due to inefficient collection and processing of both urine (containing urea nitrogen) and fecal matter. Often, only fecal matter is collected and processed. As a result, mixing animal waste with food processing waste can increase nitrogen levels which allows for optimizing the carbon:nitrogen ratio along with other nutrient ratios. This is required for maximizing methane concentration and biogas production. Biorefinery coproducts consisting of protein-rich wet distillers grains and high moisture fermentation residues can then be fed directly to animals at integrated CAFOs along with nutrient-rich food processing waste resources. Organic waste produced by animals and consumers can then be efficiently collected and processed along with algal biomass and lignocellulosic feedstocks such as water hyacinth via state-of-the-art anaerobic digestion technology, the energy efficiency for which can rival that produced by biorefineries.

Previous research reveals that combusting wet distillers grains in fluidized bed boilers to produce process steam for biorefining (thus displacing natural gas) is less efficient than first feeding it to animals and then subsequently processing animal waste and other forms of organic waste including food processing waste and municipal wastewater. There is a substantial difference in energy efficiency for thermal combustion of wet biomass vs. anaerobic digestion of the same high moisture feedstock. The following is an initial attempt to compare the life cycle analysis (LCA) and total energy efficiency for the following approaches using the same wet biomass feedstocks including freshly harvested corn stover, crop residues, lignocellulosic feedstocks, sweet sorghum, oil feedstocks and algal biomass:

1. production of advanced cellulosic biofuels such as hydrous ethanol and green gasoline from starch and lignocellulosic feedstocks
2. production of biodiesel or green diesel from feedstocks and algal biomass rich in lipids
3. production of biogas (biomethane, CO₂, ammonia) and nutrient-rich fertigation streams from the same lignocellulosic and algal biomass feedstocks used above for recycling in closed loop biomass production
4. feeding coproducts of biorefining the same feedstocks utilized above to animals for production of protein rich functional foods followed by anaerobic digestion of animal

waste, food processing waste (animal offal), and municipal wastewater (sewage) for production of biogas (biomethane, CO₂, ammonia) and nutrient-rich fertigation streams for recycling in closed loop biomass production

Such a comparative study which illustrates the technological, ecological, and economical advantages of comprehensive nutrient-energy management begins with theoretically calculating energy and organic fertilizer values followed by validation of the bioenergy potential and total bioenergy efficiency for each of the above production scenarios. Particular emphasis is placed on the ecological and economical advantages of the last two options which demonstrate maximum nutrient-energy efficiency via closed loop systems architecture.

Standard Energy Values Used in Evaluations

1 BTU = amount of heat required to increase the temperature of a pint of water (which weighs exactly 16 ounces) by one degree Fahrenheit.

1 BTU = 1,055.06 joules

100 standard cubic feet (SCF) of methane = 1,000 BTU

100 SCF of natural gas contains about 80% methane = 800 BTU

SCF =

1 MBTU of methane = 1 million BTU, 1 decatherm, or 10 therms

CH₄ = 23,895.4 HHV BTU/lb = 55.6 MJ/kg

H₂ = 61,100 HHV BTU/lb = 143 MJ/kg

1 lb of coal, = 8,100 to 13,000 HHV BTU depending on quality of coal

Since BTUs are measurements of energy consumption, they can be converted directly to kilowatt-hours: 1 Kilowatt hr of electricity = 3,414.43 BTU/hr

1 lb volatile solids (VS) = 12 cu ft of biogas (65% methane, 35% CO₂)

Terminology Used in Evaluations

Moisture: The weight of water lost upon drying at 220°F (105°C) until no more weight is lost.

Total Solids (TS): The weight of dry material remaining after drying as above. TS weight is usually equivalent to "dry weight." (However, material dried in the sun will still contain around 30% moisture.) TS is composed of digestible organic or "Volatile Solids" (VS), and indigestible residues or "Fixed Solids."

Essentially, total solids are the sum of suspended solids and dissolved solids. Total solids analyses are important for assessing wastewater treatment processes such as digester efficiencies

and sludge cake processing parameters. These tests are commonly performed on sludge samples when the concentration of solids is greater than 10,000 mg/L or 1%, thus making them very difficult to filter.

Volatile Solids (VS): The weight of organic solids burned off when dry material is "ignited" (heated to around 1000°F, 538°C). VS can be considered as the amount of solids that are biologically converted or metabolized by bacteria. VS are organic compounds of either animal or plant origin. Biological processes can metabolize and decompose these substances. VS are usually referred to as the portion of the total solids that are volatile which may or may not include volatile organic compounds prior to emission of VOC.

Volatile Organic Compounds (VOC): Is a term that refers to the portion of volatile solids that are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. For example, release of VOCs is enhanced dramatically during drying of wet distillers grains and combustion of organic waste. Volatile organic compounds are numerous and varied. Although ubiquitous in nature and modern industrial society, they may also be harmful or toxic. VOCs, or subsets of the VOCs, are often regulated by groups such as the EPA.

VOCs may be natural or synthetic. Like organic chemicals in general, there are millions of different compounds which may be classified as VOCs. The compounds that olfactory glands sense as smells are generally VOCs. Modern industrial chemicals such as fuels, solvents, coatings, feedstocks, and refrigerants are usually categorized as VOCs.

As organic chemicals, VOC may have health consequences. Because they tend toward the gaseous state, management of toxic VOCs is more difficult than with non-volatile compounds. Human exposure to VOCs can be through contact with the solid, liquid, or gaseous forms, inhalation of the gaseous form, or ingestion of the liquid form or solutions containing the VOC.

The large number of VOCs combined with their numerous exposure pathways make comprehensive management, discussion or regulation of volatile organic compounds impractical. Instead, subsets of VOCs are regulated by a wide variety of governmental agencies.

There is no clear and widely supported definition of a VOC. From a chemistry viewpoint "Volatile Organic Compound" can mean any organic compound (all chemical compounds containing carbon with exceptions) that is volatile (evaporating or vaporizing readily under normal conditions). This is a very broad set of chemicals. Definitions vary depending on the particular context. There are many other widely used terms that are a subclass of VOCs. Laws or regulations are often responsible for creation of legal definitions of VOCs or definitions of subclasses of VOCs.

Fixed Solids (FS): Weight remaining after ignition. This is biologically inert material. The fixed solids are primarily comprised of inorganic materials such as sand, gravel, and salt. These materials build up over time in digesters and must be removed along with sludge to maintain efficiency of anaerobic digestion. *In situ* processes have been developed for removing fixed solids including sludge from functioning anaerobic digesters.

COD: Chemical Oxygen Demand test commonly used to indirectly measure the amount of organic compounds in water. This is in reference to algae and plants which consume nutrients prior to dying and consuming oxygen during decomposition. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. Older references may express the units as parts per million (ppm).

The result of a relatively high COD in biological effluents which drain into natural water bodies is hypoxia. Hypoxia or oxygen depletion is a phenomenon that occurs in aquatic environments as [dissolved oxygen](#) (DO; molecular oxygen dissolved in the water) becomes reduced in concentration to a point detrimental to aquatic organisms living in the system. Dissolved oxygen is typically expressed as a percentage of the oxygen that would dissolve in the water at the prevailing temperature and salinity (both of which affect the solubility of oxygen in water; see [oxygen saturation](#) and [underwater](#)). An aquatic system lacking dissolved oxygen (0% saturation) is termed anaerobic, [reducing](#), or anoxic; a system with low concentration—in the range between 1 and 30% saturation—is called hypoxic or dysoxic. Most fish cannot live below 30% saturation. A "healthy" aquatic environment should seldom experience less than 80%. The exaerobic zone is found at the boundary of anoxic and hypoxic zones

Oxygen depletion can be the result of a number of factors including natural ones, but is of most concern as a consequence of pollution and [eutrophication](#) in which [plant nutrients](#) enter a river, lake, or ocean, [phytoplankton](#) blooms are encouraged. While phytoplankton, through [photosynthesis](#), will raise DO saturation during daylight hours, the dense population of a [bloom](#) reduces DO saturation during the night by [respiration](#). When phytoplankton cells die, they sink towards the bottom and are decomposed by bacteria, a process that further reduces DO in the water column. If oxygen depletion progresses to hypoxia, fish kills can occur and invertebrates like worms and clams on the bottom may be killed as well.

Nitrogen and phosphorus are the primary nutrients stemming from organic waste and synthetic fertilizers that are responsible for nutrient loading and eutrophication which culminate in algae blooms and subsequent hypoxia which impact the environment and contribute to pollution.

AU: Animal Unit consisting of 1,000 lbs of live animal/s

Energy Density of Lignocellulosic Biomass

1 dry ton of lignocellulosic biomass = 17.2 MBTU (8,600 HHV BTU/lb. However, the energy density of hydrogen contained in biomass is considerably higher, e.g. 20,446 HHV BTU/lb based on production of syngas utilizing gasification.

Combustion of the VS contained in 1 tonne of 70% moisture biomass (as harvested) is equivalent to: 18,963,000 BTU x .3 tonne dry matter = 5.69 MBTU/tonne (8,600 HHV BTU/lb at 30% dry matter).

Though lignocellulosic feedstocks vary considerably in composition (proportions of lignin, cellulose, hemicellulose and protein), digestibility and BTU value, the energy values listed are representative of average lignocellulosic biomass compositions. In contrast to direct combustion of biomass, BTU calculations for production of biogas from biochemical processing of biomass (fresh lignocellulosic or animal waste biomass) is based on composition of raw biogas (50-80% methane and 49-19% CO₂).

Most vegetable biomass has a different carbon to nitrogen ratio than animal waste biomass. This is due to the fact that a large majority of the volatile solids (combustible organic matter) is removed during biological digestion. Volatile solids are referred to as essential carbohydrate and lipid nutrients by nutritionists. These nutrients contained in fresh plant biomass have been removed during biological digestion prior to excretion by animals. Depending on animal diets and efficiency of collection, animal waste may be either high or low in nitrogen.

According to some estimates, on a mass basis vegetative biomass produces about eight times as much biogas as manure biomass. Hence, the quantity of undigested vegetative biomass required as an anaerobic digester feedstock is much smaller in comparison with the same volume of biogas produced from previously digested biomass. Vegetative biomass is often referred to as fibrous feedstuffs which are fed to ruminant animals such as cattle and sheep. In the biofuels/bioenergy industry, fibrous vegetative matter is usually referred to as lignocellulosic biomass. Biomass is a term also used to refer to food processing waste which is rich in carbohydrates and lipids. These sources of organic waste may have marginal nutritional value due to the complex structural nature of the carbohydrate polymers contained in lignocellulosic biomass. However, they are very good feedstocks for mixing with animal waste as substrates for anaerobic digestion.

Methane concentration in biogas can be increased to 79% without utilizing food crops or high quality biofuel feedstocks. This is accomplished from processing a variety of organic waste feedstocks, algae and water hyacinth which are relatively rich in carbohydrates and lipids ([Ghose et al., 1979](#)). Some studies reveal that utilizing the same biomass feedstock (produced on dry lands in contrast to aquatic plant species), production of biogas via anaerobic digestion can produce more energy than that which results from production of biodiesel using conventional FAME processing ([Gunaseelan, 2009](#)). For low cost production and processing of aquatic plant feedstocks such as lignin-free algae and the relatively low lignin-content of water hyacinth, energy gains would be much greater while avoiding capital and energy intensive biorefining of advanced biofuel feedstocks. Hence, organic vegetative matter such as food processing waste and algal biomass which are rich in carbohydrates and lipids are ideal feedstocks for mixing with animal waste for “low cost” production of bioenergy in the form of biogas. Biogas can then be desulfurized and utilized as a fuel cell feed, or refined into biomethane to displace natural gas consumption.

According to the information listed below for bovine animal waste, after live animals are fed fibrous feeds consisting of lignocellulosic materials, the BTU value for beef cows is 8,858 HHV BTU/lb. This value is actually 3% higher than the energy density listed above for lignocellulosic biomass. However, for dairy cows, as expected the BTU value for digested biomass is 21% lower than lignocellulosic biomass at 7,100 HHV BTU/lb. The variation in BTU values for dairy

and beef cattle is due primarily to differences in diets which are comprised of fibrous feeds (such as hay and fermentation residues – both of which are comprised of lignocellulose) and grain concentrates including distillers grains (DG). Feed to conversion efficiency is usually higher for dairy cattle than beef cattle due to superior genetic selection via use of artificial insemination. Thus, a higher proportion of volatile solids are removed from vegetative biomass by dairy cattle during ruminant digestion.

For integrated biorefineries, lignocellulosic biomass feedstocks such as corn stover (the portion of corn crops remaining after corn grain is harvested) can be used as low cost feedstocks for production of ethanol. The fermentation residue which is produced as a coproduct consists largely of quality protein feeds for ruminants which utilize microbial digestion to enhance digestibility of low cost feedstuffs. For efficient low temperature processing at biorefineries, after processing carbohydrates to sugars and biofuels, the fat and amino acid profiles of fermentation residues and distillers grains are actually three times higher than the original feedstocks. In addition, the yeast contained in the DG provides a natural feed additive which improves feed efficiency and eliminates the need for ionophores, antimicrobials which are classified as antibiotics.

Mechanical milling (shredding and chopping during harvesting), ammonia pretreatments, removal of lignin prior to fermentation, and hot water processing during distillation substantially enhances digestibility of fermentation products for use as value added animal feedstuffs. Quality of digestibility for DG and fermentation residues are actually superior to that of steam flaked corn and low quality hay. Additionally, exogenous enzymes can be fed to cattle to further enhance digestibility of both DG and fermentation residues. Feeding balanced rations of wet DG and fermentation residues at confined animal feeding operations (CAFOs) allows for reducing feed costs by about 50% for integrated operations which no longer need to dry, package or transport animal feedstuffs.

Animal waste from integration of biorefineries and CAFOs can then be processed via anaerobic digestion to provide biomethane for production of distributive generated combined cooling, heating and power (DG-CHP) via high temperature fuel cells. Thermal integration provides process steam for the biorefinery, heating of anaerobic digesters, and space heat and electricity for controlled environment agriculture (CEA). Electricity provides 24/7 lighting via low energy light emitting diode (LED) technology in order to enhance efficiency of biomass production via photosynthesis. For integrated biorefineries, total energy efficiency can exceed 90% while essentially eliminating pollution and greenhouse gas emissions (GHGEs). This allows for eliminating use of fossil fuels via closed loop architecture, provision of premium power (uninterrupted service due to failure of the power grid) additional revenue streams via grid connected power and carbon credits.

Anaerobic digestion also provides carbon dioxide and nutrient-rich effluents which provide value added fertigation streams for year round production of closed loop biomass and high value foods via CEA which includes hydroponic greenhouses and algal bioreactors. CEA and precision agriculture including subsurface drip fertigation, high density crops, and relay cropping systems can more than double conventional crop yields while eliminating nutrient run-off. The value of the organic fertilizers (including recycling of CO₂) and the biomass produced can exceed the

value of biomethane by 4-6 fold depending on the cost of natural gas and electricity. In addition, process water from biorefining and from CAFOs is recycled via integrated operations, thus reducing production requirements for irrigation water and agricultural lands.

Bovine Animal Waste

Dairy cows produce 20,600 BTU/day per AU via conventional anaerobic digestion of animal waste ([Chastain et al., 1999](#); [Cuéllar and Webber, 2008](#))

1 dry ton of dairy cattle manure = 17.07 HHV MBTU (7,100 HHV BTU/lb). However, the energy density of hydrogen contained in this biomass resource is considerably higher, e.g. 16,880 HHV BTU/lb. This is based on extracting 100% of hydrogen content via production of syngas utilizing gasification by companies such as [E3 Regenesis Solutions](#))

Combustion of the VS contained in 1 tonne of 87.5% moisture dairy bovine waste (as excreted) = 17,075,500 BTU x .125 = 2.13 MBTU/tonne (7,100 LHV BTU/lb at 12.5% dry matter)

- An average dairy cow produces 85 lb of raw manure a day per 1000 lb (AU) of animal weight (not counting bedding). As excreted, manure consists of 10.4 lb total solids (TS) and approximately 8.6 lb. of volatile solids (VS).
- Thus a 1500 lb. Holstein is likely to produce, on average, 127.5 lb. of daily waste (13.23 lb. of volatile solids). This is equivalent to a conservative 23 tons of animal waste produced annually per dairy cow.
- This waste contains on average 0.7% phosphorous, 3.9% Nitrogen and 2.6% potassium, which can be converted to chemical components for producing organic fertigation streams via closed loop biomass and controlled environment agriculture (CEA).
- In terms of hydrogen content, dairy manure averages 2,110 BTU per wet pound (87.5% moisture), which is equivalent to almost 0.618 kwh of electricity. One kwh is equivalent to 3,414 BTU.
- Thus, each cow produces the equivalent of 80 kwh per day and 2 MWh per month.
- At 35% energy efficiency for gasification of dry (animal waste) biomass this is equivalent to producing 827 kWh per month per cow or 590 kWh per AU per month.
- At 90% total energy efficiency for state-of-the-art anaerobic digestion of high moisture animal waste biomass as excreted (12.5% dry matter), including efficient collection and use of biomethane in high temperature fuel cells, this would be equivalent to theoretically producing up to 26 MBTU annually per AU, which at 47% electric efficiency is equivalent to 298 kWh and .932 MBTU of heat for thermal integration per month per AU. In addition, each AU would produce enough organic nutrients (not including CO₂) to annually produce 11.2 tons of biomass.

Fattened Beef cattle produce 25,700 BTU/day per AU via conventional anaerobic digestion of animal waste ([Chastain et al., 1999](#); [Cuéllar and Webber, 2008](#))

1 dry tonne of beef cattle manure = 19.53 MBTU (8,858 HHV BTU/lb). However, the energy density of hydrogen contained in this biomass resource is considerably higher, e.g. 21,059 HHV BTU/lb. This is based on extracting 100% of hydrogen content via production of syngas utilizing gasification by companies such as [E3 Regenesis Solutions](#)).

1 tonne of 87.5% moisture beef cattle waste (as excreted) = $19.53 \times .125 = 2.44$ MBTU (8,858 HHV BTU/lb at 12.5% dry matter)

Adding Value via Integrated CAFO Operations

Regarding economics, integration of CAFOs with AD, SDF and innovative crop production utilizing precision agriculture will increase annual revenues by up to \$895 per AU. Though many CAFOs may not own sufficient land to utilize all of the nutrients they produce, share cropping with neighboring land owners and cooperatives are commonly utilized in agricultural communities for the mutual benefit of all involved.

Integration of livestock and crop production provides much needed diversification, adds substantial value, and provides additional revenue streams for sustainable agriculture while simultaneously reducing harmful ammonia and greenhouse gas emissions. For integrated operations, the following illustrates the value of additional revenue streams via savings per AU and per acre. The calculations include current and future carbon credits highlighted in red which are subject to verification for trading on the [Chicago Climate Exchange \(CCX\)](#) and eventually the European Union Exchange.

Revenue per AU (US EPA Air Emissions Inventory 2005):

- About 10-13 MBTU (10,000-13,000 cu ft) of biomethane annually via AD=about \$70-\$100 (ranges from \$73-\$141 depending on type of animal, efficiency of waste collection system, anaerobic digester technology, and natural gas prices)
- Enough nutrients to produce 200 bu of corn annually=about \$685 @ \$4/bu, \$885 @ \$5/bu, and \$1,085 @ \$6/bu which includes deducting crop expenses calculated below
- About 465 lbs of organic compost annually=wholesale value about \$5
- About 1580 lbs of CO₂=about \$80
- GHGE Reductions Credits for AD is about 2.5 Carbon Credits (Calvin) @ \$4/carbon credit=\$10; \$5/carbon credit=\$12.50
- Potential GHGE ammonia (NH₃) credits is about 1.26 carbon credits @ \$4/carbon credit = \$5.04; \$5/carbon credit = \$6.30
- Potential GHGE CH₄ carbon credits via NFE ([Nkrumah et al 2006](#)) & Diet ([McGinn et al 2004](#)) = about .89 carbon credits @ \$4/carbon credit =about \$3.53; @ \$5/carbon credit = about \$4.45 (GHGE)
- Potential GHGE N₂O credits via NFE & Diet= 1.48 carbon credits @ \$4/carbon credit=about \$5.94; @ \$5/carbon credit = \$7.40 (Takahashi & Young, 2002)
- **Additional Annual Income per AU for CAFOs = about \$895 based on \$4/bu corn, \$1,095 @ \$5/bu corn, and \$1,295 @ \$6/bu corn**

The above estimates are based on averages for feedlot cattle. Lactating dairy cows will increase the carbon credits available per AU, but decrease the rate of improvement for NFE (net feed efficiency). Most dairies calculate 10 MBTU per AU in order to allow for dry cows and inefficient animal waste collection systems. As illustrated above, carbon credits and NH₃ credits provide significant economic incentives for invoking positive change.

Optimizing Heterosis & Breed Complimentarity for Livestock Production

Similar to optimizing biomass production via hybrids, the same is true for development of superior livestock and poultry hybrids, i.e. crossbred species which enhance heterosis and breed complementarity.

Bovine species which provide the most potential for optimizing heterosis and breed complementarity are those species and breeds which have the most diversity. According to several studies of *Bos indicus* and *Bos taurus* crossbreeds, heterosis can average over 50% (individual and maternal heterosis combined) in crossbreeding programs. According to MARC geneticist Larry Cundiff (2007), this large heterosis effect is due partially to lack of environmental adaptability for British and Continental cattle which are transplanted into subtropical or tropical environments, and hence perform poorly when compared to tropically adapted *Bos indicus* breeds.

In temperate environments, British x Continental crossbreeding provide superior carcass traits, net feed efficiency, early puberty and exceptional maternal ability which results in 24%-26% total heterosis. According to MARC-USDA research, British x Continental heterosis can increase weight of calf weaned per beef cow exposed by 20%-26%. Cross bred beef cows remain in the herd 1.3 years longer and have a 30% greater lifetime production than straight bred cows (Cundiff et al., 1999).

Balanced nutrition, marker assisted selection indexes, advances in reproductive physiology, crossbreeding, innovative forage production, and intense grazing management can subsequently increase stocking rates and conventional livestock production by over two fold (Peck; Thoney; Gregory et al., 1990; Echtenkamp et al., 2007; Kirkpatrick, 2002; Patterson et al 2007).

Preserving Nutrients via Efficient Collection & Anaerobic Digestion of Animal Waste

Nutrient content of manure from dairy cattle is affected by a variety of factors, many of which are related to a specific farming operation. Some of these factors include method of storage, type of manure application system, housing and bedding system, diet of the cattle and environmental temperature. Diet of the animals and efficiency of collection and processing are usually the most important factors. However, all of these factors affect the amounts of nitrogen (N), phosphorus (P), potassium (K) and micronutrients in the manure, as well as its net value.

Tables are available that estimate the amount of nutrients in animal manure. Since each accumulation of manure is unique, the table values are only meant to be approximate and variations are expected. Table 5 contains values from liquid and solid manure handling systems for dairy cattle. Since several thousand pounds or gallons of manure are applied per acre, small deviations caused by under- or overestimations of the composition of manure can result in significant differences in nutrients when utilized as organic fertilizers.

Table 5. Average nutrient composition of manure from dairy cattle.

Handling system	Nutrients (lbs/ton)		
	N	P ₂ O ₅	K ₂ O
Solid system	11	5	11
Semi-liquid	5 (26) ¹	2 (11)	4 (23)

¹lbs/1,000 gallons

(Midwest Plans Publication Number #1 - 1983 Edition; [Pennington et al., 2009](#))

The most reliable and accurate way to determine the nutrient content of a particular farm's manure is to have a sample of the manure analyzed by a laboratory. This method eliminates the numerous approximations made by using table values. Most soil testing laboratories do manure testing for a nominal charge. The ideal time to sample the manure is just prior to or at spreading. For liquid manure systems, it is important that the pit be agitated vigorously before sampling so samples of top water and settled solids are blended, while for solid manure, several cores should be taken throughout the manure. Good sampling procedures are necessary since the nutrients in manure are not distributed evenly between the liquid and solid portions. Dried manure has organic matter and composition similar to very poor quality hay (Table 6).

Table 6. Composition of dried manure.¹

Component	% of Dry Matter
Ash	13.3-13.4%
Nitrogen	1.2-1.6%
Non Detergent Fiber (NDF)	77.7-83.5%
Acid Detergent Fiber (ADF)	50.5-52.7%
Cellulose (ADF-ADL ²)	35.4%
Hemicellulose (NDF-ADF)	32.0%

¹ Similar to poor quality hay

² Acid Detergent Lignin

(Midwest Plans Publication Number #1 - 1983 Edition; [Pennington et al., 2009](#))

Dairy cows excrete 223-260 lbs N, 40-69 lbs P₂O₅ and 88-146 lbs K₂O per year in manure, depending on many factors but primarily based on volume of consumption, composition of feedstuffs, and feed to conversion efficiency of the animal. In total, the value of the organic fertilizers may be almost \$300 per 1,400 lb cow each year (Table 7), or \$210 per animal unit (AU) (Table 8).

Table 7. Amount and value of manure/dairy cow.

223-260 lbs N @ \$0.72/lb	N = \$174
40-69 lbs P ₂ O ₅ @ \$0.58/lb	P ₂ O ₅ = \$32
88-146 lbs K ₂ O @ \$0.75/lb	K ₂ O = \$88
Total value	\$294/cow/year potential value

(Midwest Plans Publication Number #1 - 1983 Edition; [Pennington et al., 2009](#))

Table 8. Amount and value of manure/animal unit (AU).

159-186 lbs N @ \$0.72/lb	N = \$124
29-49 lbs P ₂ O ₅ @ \$0.58/lb	P ₂ O ₅ = \$23
63-104 lbs K ₂ O @ \$0.75/lb	K ₂ O = \$63

Total value	\$210/AU/year potential value
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Adapted from Midwest Plans Publication Number #1 (1983 Edition)
([Pennington et al., 2009](#))

However, due to loss of nitrogen content from urine/urea hydrolysis, volatility of ammonium/ammonia nitrogen, and mineralization, not all of these nutrients are available for use as nutrients on crops during the first year of land application. This is particularly true for N. Additionally, depending on efficiency and precision of land applications, nutrients such as P and K may be of adequate levels in the soil, which will decrease their economic value in the manure. Moreover, in select cases, P may exceed recommended levels in the soil and should not be applied to soil, either as manure or commercial fertilizer. However, providing balanced diets for livestock and poultry, efficient animal waste collection, and state-of-the-art anaerobic digestion can preserve 90-95% of nutrients and bioenergy (volatile solids/organic compounds) contained in animal waste.

Table 9. Composition and estimated uptake of nutrients by crops (per ton of dry matter).

Crop	Composition (% DM)			Nutrient Uptake Per Acre (lbs)		
	Crude Protein	P	K	N	P ₂ O ₅	K ₂ O
Alfalfa ^{1,2}	20.8	0.34	2.80	333	78	337
Bermuda ¹	14.6	0.21	1.92	234	48	231
Corn Silage ¹	8.3	0.27	1.22	133	62	147
Fescue ¹	9.8	0.30	2.51	157	69	302
Sorghum ¹ Forage	7.9	0.32	1.80	126	73	217
Soybean ^{1,2} Forage	15.8	0.47	1.04	253	108	125
Cotton ^{3,4}	--	--	--	176	52	154
Rice ^{3,5}	--	--	--	112	60	168
Soybean Grain ^{2,3,6}	--	--	--	288	53	188

¹ Assuming 5 ton DM yield/acre

² A legume which can fix nitrogen from the air and does not require all N as fertilizer

³ Plant is usually separated into seed and other products, some of which may be left on the land.

⁴ Assuming 1,100 lb yield/acre

⁵ Assuming 7,000 lb yield/acre

⁶ Assuming 55 bu yield/acre

(Midwest Plans Publication Number #1 - 1983 Edition; [Pennington et al., 2009](#))

Utilizing an efficient animal waste collection system in conjunction with state-of-the-art anaerobic digestion, nitrogen and other essential nutrients can be conserved and applied to soil and crops much more efficiently than conventional animal waste management and land application systems.

According to Iowa research data, a typical dairy herd produces 32.77 tons of solid manure per milk cow per year. Notice that this estimate is almost three tons more than the data listed above. (See Iowa State University Extension publication Pm 1811, Managing manure nutrients for crop production.) For example, a 75 cow dairy and replacements create 2,458 tons of manure per year.

For this land application example, assume that 85% of manure is collected and surface-applied on 130 acres of cropland. The 2,089 tons of manure to be spread has an analysis of 12-6-12 (N-P-K, and 70% of the N will be available to the crop after in-field volatilization. (See Pm 1811.) If 50% of the N will be available to the crop the first year, there will be 8,774 pounds of N; 12,534 pounds of P; and 25,068 pounds of K credited for crop use if soils are testing in the optimum range or lower ([Ingles, 2006](#)).

According to the above land application model, about 50% of nitrogen is lost due to inefficient collection and in-field volatilization shortly in the first year. For anaerobic digestion and subsequent use of effluents as valued added liquid fertilizers as for integration of SDF systems, over 90% of the nitrogen lost in land applications is conserved. Hence, with anaerobic digestion and SDF, 17,548 lbs of N; 12,534 lbs of P; and 25,068 lbs of K are available for crop use. The value of these organic fertilizers including secondary macronutrients and micronutrients is in addition to the value of the methane and CO₂ produced by anaerobic digestion.

Efficient Animal Waste Management Systems

Planning proper waste handling not only helps protect the environment, it can improve the overall farming operation and overall cash flow. For example, dairymen who add freestalls not only provide for closed loop waste handling but also provide shade, feeding and loafing areas for the animals. These improvements translate into more milk (and easier management) which normally pays for the construction cost in 3 to 5 years.

The following table lists the nutrients in animal waste (N, P, K) for various animals based upon a 1,000 pound animal unit over a period of one year.

Table 10. Annual Pounds of Nutrients in Manure as Excreted per 1000 Pounds Live weight

	Dairy Cow	Beef Feeder	Swine Feeder	Laying Hen	Broiler
Nitrogen, N	150	124	164	263	423
*Phosphate, P₂O₅	60	91	124	232	216
*Potash, K₂O	118	106	132	136	158

* Elemental P & K conversion can be made as follows: To convert P₂O₅ to elemental P, multiply by 0.44; and to convert K₂O to elemental K, multiply by 0.83.

(Midwest Plans Publication Number #1 - 1983 Edition; [Pennington et al., 2009](#))

Method of Handling & Land Application

Average nitrogen losses which occur with various manure handling and storage methods are provided in Table 11.

Table 11. Nitrogen Losses from Manure as Affected by Handling and Storing Methods

Handling, Storing Methods	Nitrogen Loss*
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Solids Systems:	
Manure Pack	35%
Poultry Litter	35%
Liquid Systems:	
Anaerobic Digester	<5%
Anaerobic Pit	25%
Oxidation Ditch	60%
Lagoon	80%
* Based on composition of manure applied to the land vs. composition of freshly excreted manure.	

Table 12. Nitrogen Loss from Manure to the Air as Affected by Application Method

Application Method	Type of Manure	Nitrogen Loss*
SDF (sub-surface drip fertigation)	Liquid	<5%
Broadcast without cultivation	Solid	20%
	Liquid	25%
Broadcast with cultivation**	Solid	5%
	Liquid	5%
Knifing	Liquid	5%
Irrigation	Liquid	30%
* Percent of total nitrogen in manure applied that was lost within 4 days after application		
** Cultivation immediately after application.		

While the above data may be useful for approximation, laboratory analysis of the waste and soil test is the best approach to insure optimal nutrient ratios and maximum crop yields ([Hammond, 2005](#)).

Precision Agriculture: SDF, High Density Relay Cropping Systems

For purposes of illustration via anaerobic digester effluents, a 1,000 cow dairy could provide enough fertilizers for production of over 2,000 acres of conventional crops. Utilizing high plant density, no-till planting and double cropping systems via SDF, the same amount of crops could

be produced on less than 1,000 acres using 40-60% less water, 80% less fertilizers, and 50% less fuel in comparison with conventional crop production.

The following is an example of the nutrients contained in the influents and effluent of an IBR anaerobic digester which could be utilized as value added organic fertilizers for SDF systems.

Table 13. IBR Nutrient Analysis of Dairy Effluent

IBR-AD System	Influent	Effluent	Effluent after the Screw Press	%
pH	7.54	7.6	7.8	n/a
Electrical Conductivity, dS/m	16.4	16	16.1	n/a
Nitrogen (N), %	0.31	0.23	0.22	.22
Phosphorus (P), mg/L	488.4	416	411.4	.04114
Potassium (K), mg/L	1979.2	1734.4	1798.7	.17987
Calcium (Ca), mg/L	1840.5	1497.3	1450.7	.14507
Magnesium (Mg) mg/L	744	772.9	725.3	.07253
Sulfur (S) mg/L				
Sodium (Na), mg/L	435	413.4	392.6	.03926
Boron (B), mg/L	4.1	3.3	3.13	.000313
Zinc (Zn), mg/L	10.78	9.44	9.0	.0009
Copper (Cu), mg/L	77.94	56.76	61.91	.006191
Iron (Fe), mg/L	117.07	99.28	95.34	.009534
Manganese (Mn), mg/L	11.52	10.21	10.07	.00107

Influent: Manure that has not yet entered the digester.

Bottom Sludge: Manure at the bottom of a digester tank.

Effluent: Manure that has been through the digester but not through the fan separator.

Effluent after the Screw Press: Manure that has been through the digester and through the fan separator (screw press).

*Source Utah State University Soils Lab (www.usual.usu.edu)

As illustrated in the above table which was compiled using conventional chemical extraction, no values are listed for sulfur. The values listed for phosphorous are disproportionately high in comparison with the other nutrient levels including nitrogen which is disproportionately low. Additionally, it is preferable to measure ammonium and nitrate forms of nitrogen separately via ion exchange resin technology. In summary, optimizing nutrient ratios in animal diets is critical to balancing nutrients in anaerobic digester substrates and effluents. This comprehensive nutrient-energy management approach is crucial for maximizing production efficiencies for methane-rich biogas and organic fertigation streams for closed loop biomass, particularly for integrated operations.

Since corn is only about 50% efficient in regards to nutrient utilization, the amount of algal biomass produced from those same nutrients (including recycled CO₂ from anaerobic digestion), is estimated to be between 11 to 19 tons annually per AU. This is based on the fact that each AU produces over 19 tons of organic matter which can be efficiently collected and processed via state-of-the-art anaerobic digestion and conditioning of nutrient-rich biological effluents.

In summary, utilizing the majority of high quality lignocellulosic biomass first as a biofuel feedstock, second as a valued added livestock feedstuff, and third as a renewable biomass feedstock for anaerobic digestion of animal waste for production of biogas provides unprecedented production efficiencies and zero net carbon emissions via closed loop systems architecture.

Fertigation & Chemigation - BMP (Best Management Practice)

SDF, which combines fertilizer applications with irrigation practices, is a form of chemigation. Chemigation is considered a BMP by USDA and NRCS. Chemigation includes the injection of other chemicals such as soil amendments, pesticides, etc., into irrigation water and applying them through the irrigation system to crops via precision agriculture.

SDF, Chemigation & High Density Relay Cropping Systems

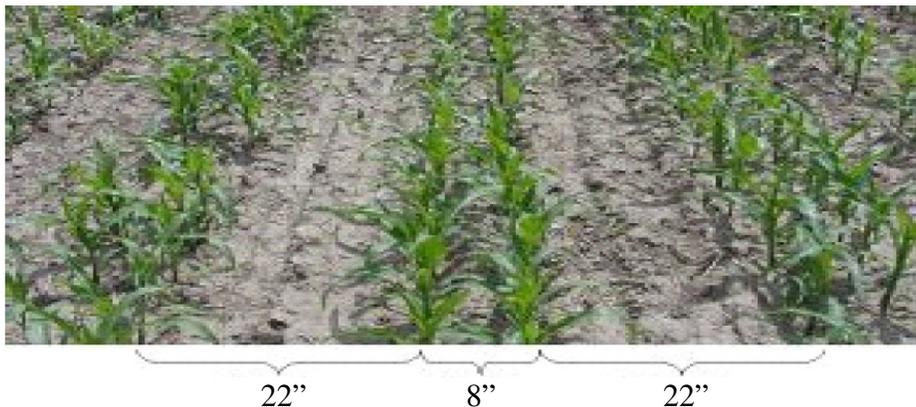


Figure 5. Twin Row Crops with 30" Lateral Drip-tube Spacing

Illustration of Advantages for SDF at a Sample Dairy Farm

When a 40% increase in irrigated lands is combined with doubling crop yields via high density planting, conservation tillage (which is complimented by SDF), and multiple cropping systems, there is potential to increase conventional crop yields by nearly three fold ($1.4 \times 2 = 2.8$). When a 70% increase in irrigated lands is combined with doubling crop yields via precision agriculture, conventional crop yields could be increased by over three fold ($1.7 \times 2 = 3.4$).

Conservation tillage combined with responsible crop residue management essentially eliminates erosion, decreases water loss due to soil evaporation, decreases nutrient run-off, and restores valuable OM (organic matter) to the soil as illustrated by the following example:

management, anaerobic digestion, and medium-low pressure irrigation systems via sub-surface drip fertigation (SDF) will result in the following economic savings per acre for either direct or indirect crop production by livestock operations:

Savings per acre ([US EPA Air Emissions Inventory 2005](#)):

- Conservation tillage results in saving 3.5 gallons of diesel, valued at \$2.50 per gallon=\$8.75 (1.75% reduction in production costs)
- Conservation tillage carbon credits=\$0.16 (Burning 1 gallon of diesel releases 22.384 lbs of CO₂, so 1 metric ton of CO₂ is released for each 98 gallons of diesel used. 3.5 gallons per acre savings for no-till produces .039 tons CO₂, i.e. about 4 tons/100 acres.)
- Conserving animal waste nutrients plus 25% less nutrients required by SDF=\$106 (21.20% reduction in production costs)
- Carbon credits for conserving N ([Walters 2006](#)) and CO₂=about \$1.68
- **Potential GHGE carbon credits for conserving N₂O=about ?** ([McSwiney & Robertson 2005](#))
- Medium-low pressure SDF system=about \$20
- 30-60% improvement in water conservation via SDF (4x8 gallons diesel)=\$80-120 (24% reduction in production costs)
- Carbon credits for reducing diesel/power for pumping water=about \$1.80
- SDF and precision agriculture for conserving nutrients=\$13
- Pesticide management and reduced herbicides with high density planting and SDF=\$40 (8% reduction in production costs)
- **Total savings per acre = \$270-\$370** (This represents a 56% reduction in production costs not including labor.) Typical costs for producing corn per acre, estimated at \$500-600 (after adjusting for fuel and fertilizer price increases), minus \$270-\$370 in conservation savings equals about \$230-\$330 total production costs per acre ([USDA Economic Research Service 2001](#)).

At \$330 per acre for 400 bu of corn, this equates to \$0.83/bu. Allowing for 30% of production expenses attributed to energy, labor and material input costs, integrated operations can process corn into ethanol for less than \$0.40 gal. When the value of coproducts such as DG products, livestock production, and the potential for CEA such as hydroponic greenhouses and algal photobioreactors are considered, the revenues generated from processing crop residues via ruminant livestock, anaerobic digestion and integrated biorefineries exceeds the production efficiencies which are possible for cellulosic fermentation of crop residues to ethanol. However, processing the entire plant via integration of starch and cellulosic feedstocks at integrated biorefineries is the most efficient use of biomass.

The result of the above reductions in production costs and additional revenue streams provide unprecedented efficiencies of operation for integrated livestock operations which produce livestock feeds, consumer foods, biofuel feedstocks, and other agricultural crops from animal/organic waste.

In addition to integration with CAFOs, similar increases in revenue streams and adding value to processing via comprehensive nutrient-energy management could be achieved by integrating

biorefineries, food processors, and municipal wastewater treatment facilities with crop/biomass production.

Since the cost of diesel fuel and fertilizers continues to increase production costs, the most effective method of calculating total reductions in production costs due to SDF and precision cropping systems is via the following percentages of costs based on US EPA air emissions inventory and USDA production costs per acre:

- Diesel Conservation
 - Conservation tillage & harvesting: 1.75%
 - Irrigation water pumping: 24%
- Fertilizer Conservation
 - 25% decrease in organic fertilizers: 21.20%
 - 80% decrease in synthetic fertilizers: 25%
- 50% decrease in pesticides: 8%
- Savings via carbon credit revenues: 1%
- Total possible reduction in production costs for integrated operations which process organic waste, estimated per unit of crop produced = as much as 81% including labor.

The result of the above reductions in production costs and additional revenue streams provide unprecedented efficiencies of operation for integrated operations by processing organic waste into biofuels and fertilizers. In addition to producing biomethane, ethanol can be produced from corn, triticale, water hyacinth and algal biomass for less than \$.50/gal while simultaneously reducing GHGE.

Carbon to Nitrogen Ratio (C/N) Essential for Optimizing Methane Production

The amount and characteristics of organic materials (both plant and animal wastes) available for digestion vary widely. In rural areas, the digestible material will depend upon the climate, the type of agriculture practiced, the animals used and their degree of confinement, the methods of collecting wastes, etc. There are also degrees of quality and availability unique to urban wastes. Due to these variables, it is practically impossible to devise or use any formula or rule-of-thumb method for accurately determining the amount and quality of organic wastes to be expected from any given source. There is, however, some basic information which is useful determining optimal feedstocks for use in an anaerobic digester.

From a biological point of view, digesters can be considered as a culture of bacteria feeding upon and converting organic wastes. The elements carbon (in the form of carbohydrates) and nitrogen (as protein, nitrates, ammonia, etc.) are the chief foods of anaerobic bacteria. Carbon is utilized for energy and the nitrogen for building cell structures. These bacteria use up carbon about 30 times faster than they use nitrogen. Hence, optimizing nutrient ratios via mixed substrates can substantially enhance efficiency of digestion and methane concentration of biogas produced.

Anaerobic digestion proceeds best when raw material fed to the bacteria contains a certain amount of carbon and nitrogen together. The carbon to nitrogen ratio (C/N) represents the proportion of the two elements. A C/N ratio of 30 (C/N = 30/1, 30 times as much carbon as nitrogen) will permit digestion to proceed at an optimum rate provided other conditions are favorable (pH, temperature, solids loading rate). If there is too much carbon (high C/N ratio; 60/1

for example) in the raw wastes, nitrogen will be used up first, with carbon left over. This will decrease efficiency of anaerobic digestion, reduce biogas production rate, and decrease methane concentration. On the other hand, if there is too much nitrogen (low C/N ratio; 30/15 for example), the carbon soon becomes exhausted and fermentation stops. The remaining nitrogen will be lost as ammonia gas (NH_3) which is undesirable. This loss of nitrogen decreases the fertility of the effluent and sludge. Hence, optimizing C:N ratios using mixed feedstocks for anaerobic digesters can maximize quantity and quality of biogas produced. This process will also minimize production of ammonia and preserve nitrogen in an aqueous state for conditioning and use as a value added fertigation stream for closed loop production.

There are many standard tables listing the C/N ratios of various organic materials, but they can be very misleading for at least two reasons:

- The ratio of carbon to nitrogen measured chemically in the laboratory is often not the same as the ratio of carbon to nitrogen available to the bacteria as food (some of the food could be indigestible to the bacteria; straw, lignin, etc.).
- The nitrogen or carbon content of even a specific kind of plant or animal waste can vary tremendously according to the age and growing conditions of the plant; and the diet, age, degree of confinement, etc., of the animal.

Nitrogen: Because nitrogen exists in so many chemical forms in nature (ammonia- NH_3 ; nitrates, NO_3 ; proteins, etc.), there are no reliable "quick" tests for measuring the total amount of nitrogen in a given material. One kind of test might measure the organic and ammonia nitrogen (the Kjeldahl test), another might measure the nitrate/nitrite nitrogen, etc. Also, nitrogen can be measured in terms of wet weight, dry weight or volatile solids content of the material; all of which will give different values for the proportion of nitrogen. Finally, the nitrogen content of a specific kind of manure or plant waste can vary, depending on the growing conditions, age, diet, and so forth.

For example, one study reported a field of barley which contained 39% protein on the 21st day of growth, 12% protein on the 49th day (bloom stage), and only 4% protein on the 86th day (Rubins and Bear, 1942).

The nitrogen content of manure also varies a great deal. Generally, manures consist of feces, urine and any bedding material (straw, corn stalks, hay, etc.) that may be used in the livestock shelters. Since urine is excreted as the method for the animal to reduce excess nitrogen, the nitrogen content of manures is strongly affected by how much urine is collected with the feces.

For example, birds naturally excrete feces and urine in the same load, so that the nitrogen content of chickens, turkeys, ducks, and pigeons are highest of the animal manures in nitrogen content. Next in nitrogen content, because of their varied diets or grazing habits are humans, pigs, sheep, and then horses. However, once human excretions are combined with food waste, etc., nitrogen content increases substantially in the sludge contained in sewage. Cattle and other ruminants (cud chewers) which rely on bacteria in their gut to digest plant foods, have a low content of manure nitrogen because much of the available nitrogen is used to feed their intestinal bacteria (Figure 7).

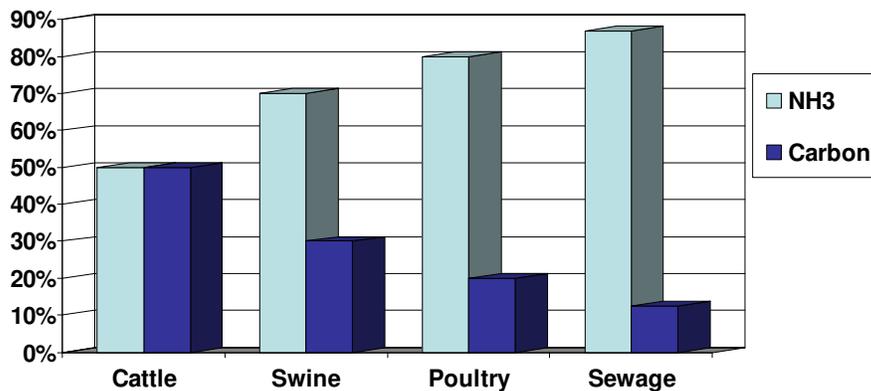


Figure 7. Ratios of Nitrogen & Carbon (organic matter) in Types of Organic Waste.

Even with the same kind of animal there are big differences in the amount of manure-nitrogen. For example, stable manure of horses may have more nitrogen than pasture manure because feces and urine are excreted and collected in confined areas. This is an advantage for CAFOs which can efficiently collect both feces and urine and continually routed directly to the digester via gravity feed systems.

Since there are so many variables, and because anaerobic bacteria can use most forms of nitrogen, the available nitrogen content of organic materials can best be generalized and presented as total nitrogen (% of dry weight).

Carbon: Unlike nitrogen, carbon exists in many forms which are not directly useable by bacteria and other microbes. The most common indigestible form of carbon is lignin, a complex plant compound which makes land plants rigid and decay-resistant. Lignin can enter a digester either directly with plant wastes themselves or indirectly as bedding or undigested plant food in manure. Thus, a more accurate picture of the C part of the C/N ratio is obtained when we consider the "non-lignin" carbon content of plant wastes.

Calculating C/N Ratios

Table 14 can be used to calculate roughly the C/N ratios of mixed raw materials. Consider the following examples:

Example 1

Calculate the C/N ratio of 50 lbs horse manure (C/N=25) and 50 lbs dry wheat straw (C/N=150).

Nitrogen in 50 lbs horse manure = 2.3% x 50 = 1.2 lbs

Carbon in 50 lbs horse manure = 25 times more than nitrogen = 25 x 1.2 = 30 lbs

Nitrogen in 50 lbs wheat straw = 0.5% x 50 = .25 lbs

Carbon in 50 lbs wheat straw = 150 times more than nitrogen = 150 x .25 = 37.5 lbs

	Manure	Straw	Total
-			

Carbon	30	37.5	67.5 lbs
Nitrogen	1.2	.25	1.45 lbs
C/N ratio = 67.5/1.45 = 46.5			

Although a bit high, this would be a satisfactory ratio for most digestion purposes.

Example 2

Calculate the C/N ratio of 8 lbs grass clippings (C/N=12) and 2 lbs of chicken manure (C/N=15).

Nitrogen in 8 lbs grass clippings = 4% x 8 = .32 lbs

Carbon in 8 lbs grass clippings = 12 times more than nitrogen = 3.8 lbs

Nitrogen in 2 lbs chicken manure = 6.3% x 2 = .13 lbs

Carbon in 2 lbs chicken manure = 15 times more than nitrogen = 1.9 lbs

-	Manure	Grass	Total
Carbon	3.8	1.9	5.7
Nitrogen	0.32	0.13	0.45
C/N ratio = 5.7/.45 = 12.6			

The C/N ratio of this mixture is low. We might want to add a higher proportion of chicken manure since it contains more carbon per weight than the grass.

The following table is a summary of the important chemical properties of organic waste materials. Values listed are averages derived from a variety of sources and should be used only for approximation subject to sampling of actual feedstocks ([Fry, 2009](#)).

Table 14. Carbon & Nitrogen Values of Wastes		
-	Total Nitrogen % Dry weight	C/N Ratio
Animal Wastes		
Urine	16	0.8
Blood	12	3.5
Bone Meal	-	3.5
Animal Tankage/Offal	-	4.1*
Dry Fish Scraps	-	5.1*
Manure		
Human feces	6	6-10
Human urine	18	-

Chicken	6.3	15
Sheep	3.8	-
Pig	3.8	-
Horse	2.3	25*
Cow	1.7	18*
Sludge		
Milorganite	-	5.4*
Activated	5	6
Fresh Sewage	-	11*
Plant Meals		
Soybean	-	5
Cottonseed	-	5*
Peanut Hull	-	36*
Plant Wastes		
Hay, Young Grass	4	12
Hay, Alfalfa	2.8	17*
Hay, Blue Grass	2.5	19
Seaweed	1.9	19
Non-Legume Vegetables	2.5-4	11-19
Red Clover	1.8	27
Straw, Oat	1.1	48
Straw, Wheat	0.5	150
Sawdust	0.1	200-500
Nitrogen is total nitrogen dry weight and carbon is either total carbon (dry weight) or (*) non-lignin carbon (dry weight).		

Table adapted from [Fry, 2009](#).

Biogas Composition

The gas produced by anaerobic digestion, known commonly as biogas, varies from 55%-80% methane (CH₄) and 19-44% carbon dioxide (CO₂) with insignificant traces of oxygen and sulfurated hydrogen (H₂S) which gives the gas a distinct odor. (Although it smells like rotten eggs, this odor has the advantage of being able to trace leaks easily.)

The basic gas producing reaction in the digester is: carbon plus water = methane plus carbon dioxide (2C + 2H₂O = CH₄ + CO₂). The methane has a specific gravity of 0.55 in relation to air. In other words, it is about half the weight of air and so rises when released to the atmosphere. Carbon dioxide is more than twice the weight of air, so the resultant combination of gases, or

simply biogas, when released to atmosphere, will rise slowly and dissipate.

CH ₄	methane	54 - 70%
CO ₂	carbon dioxide	27 - 45%
N ₂	nitrogen	0.5 - 3%
H ₂	hydrogen	1 - 10%
CO	carbon monoxide	0.1%
O ₂	oxygen	0.1%
H ₂ S	hydrogen sulfide	trace

Biofuel Value

The fuel value of bio-gas is directly proportional to the amount of methane it contains (the more methane, the more combustible the bio-gas). This is because the gases, other than methane, are either non-combustible, or occur in quantities so small that they are insignificant. Since tables of "Fuel Values of Bio-Gas" may not show how much combustible methane is in the gas, different tables show a wide variety of fuel values for the same kind of gas, depending on the amount of methane in the gas of each individual table.

Fuel gas	Fuel value (BTU/ft ³)
Coal (town) gas	450-500
Bio-gas	540-700
Methane	896-1069
Natural gas (methane or propane-based)	1050-2200
Propane	2200-2600
Butane	2900-3400

The composition and fuel value of biogas from different kinds of organic wastes depend on several things:

- The temperature at which digestion takes place.
- The nature of the raw material. According to Ram Bux Singh (1971a, 1971b): "pound for pound, vegetable waste results in the production of 7 times more gas than animal waste." In our experience, pressed plant fluids from succulent plants (cactus), greatly increases the amount of gas produced, but certainly not by a factor of 7. [Harold Bate](#) (the chicken manure car) has noted that more gas is produced from manure with a little straw added. But, we are more interested in the production of methane than biogas. Some laboratory experiments (Ref. 40, 41) have shown that plant materials produce biogas with a high proportion of carbon dioxide. So, the extra gas produced by plants may be less valuable for our purposes of fuel production.

The general quality of biogas can be estimated from the C/N ratio of the raw materials used.

		Methane	CO ₂	Hydrogen	Nitrogen
C/N Low (high nitrogen)	blood, urine	little	much	little	much
C/N High (low nitrogen)	sawdust, straw, sugar and starches such as potatoes, corn, sugar beet wastes	little	much	much	little
C/N Balanced (C/N = near 30)	manures, garbage	much	some	little	little

With good temperature and raw materials, 50 to 70% of the raw materials fed into the digester will be converted to bio-gas.

Amount of Biogas From Different Wastes

The actual amount of gas produced from different raw materials is extremely variable depending upon the properties of the raw material, the temperature, the amount of material added regularly, etc. Again, for general rule-of-thumb purposes, the following combinations of wastes from a laboratory experiment can be considered as minimum values:

Material	Proportion	Ft ³ Gas Per lb VS Added	CH ₄ Content of Gas (%)
Chicken Manure	100%	5.0	59.8
Chicken Manure & Paper Pulp	31% 69%	7.8	60.0
Chicken Manure & Newspaper	50% 50%	4.1	66.1
Chicken Manure & Grass Clippings	50% 50%	5.9	68.1
Steer Manure	100%	1.4	65.2
Steer Manure & Grass Clippings	50% 50%	4.3	51.1

Other values for gas production are from working digester operations. These are shown as cubic feet of gas produced by the Total Solids and are more liberal values than in Table 19.

Manure	Ft ³ /lb of Dry Matter (TS)
Pig	6.0 - 8.0
Cow (India)	3.1 - 4.7
Chicken	6.0 - 13.2

Conventional Sewage	6.0 - 9.0
(Fry, 2009)	

As an example, suppose we had 100 chickens which were allowed to forage during the day, but were cooped at night, so that only about half of their manure was collectable. At 0.1 lb/chicken/day this would amount to about 10 lbs of wet or 3.5 lbs dry (Table 19) manure per day. Other conditions being equal, this could be equivalent to about 20-40 ft.³ of biogas. At 60% methane it would be equivalent to 12-24 ft.³ of methane gas per day; at 80% methane, it would be equivalent to 16-32 ft.³ of methane per day.

Economic Value of Energy & Products Produced via Processing Municipal Wastewater

(Data is calculated *per capita* estimated at 20% of an AU)

Savings per capita: ([US EPA Emissions Inventory 2005](#))

- About 2-2.6 MBTU (2,000-2,600 cu ft) of biomethane annually via AD = about \$17-20
- Enough nutrients to produce 40 bu of corn annually = \$120 @ \$3/bu, \$160 @ \$4/bu, \$200 @ \$5/bu, \$240 @ \$6/bu
- About 316 lbs of CO₂ = about \$16
- GHGE Reductions Credits for AD = about .5 Carbon Credits @ \$4/carbon credit = \$2; @ \$5/carbon credit = \$2.50
- **Annual Income per capita = about \$198**

In general, a wastewater treatment facility (WWTF) with a total influent flow rate of 4.5 MGD (million gallons per day) can produce approximately ([US EPA CHP Partnership; Municipal Wastewater Treatment Facilities](#)):

- 100 kilowatts (kW) of electricity to offset purchased electricity or sell to the grid.
- 12.5 million British thermal units (BTU) per day of thermal energy that can be used as heat for an anaerobic digester and/or for space heating loads such as CEA which includes algal photobioreactors.

Based on using an average 100 GPD (gallons per day) *per capita*, 4.5 MGD is produced by a population of 45,000. Hence, 2.22 watts and 125 BTU could be produced daily *per capita*. Annually, this equates to 811 watts plus 101,470 BTU via thermal integration produced *per capita* for conventional CHP applications. Using the methane by-product from processing the sewage of 650,000 Seattle area residents, those at the South Treatment Center in Renton, WA have powered a 1 MW fuel cell plant at about 43% electric efficiency ([King County Fuel Cell Demonstration Project](#)).

At 90% total energy efficiency for integration of a high rate anaerobic digester, biogas refining, CHP-MCFC application (Municipal Energy Complex) power generation could be increased by almost 2 fold, i.e. by about 1,600 watts and 200,000 BTU (via thermal integration) annually *per capita*. By reducing water consumption to 30 GPD *per capita*, the solids ratio would increase to about 6%. AD capacity would be decreased by up to 70% which would reduce capital expenses proportionately while maintaining efficiency of biomethane production.

The ability to enhance wastewater processing via high rate AD (low hydraulic retention time) depends on the following conditions:

- Separation of industrial waste chemicals from organic matter derived from domestic wastewater (this is legally required and enforced by EPA)
- Increasing solids ratio via conservation of water and having the ability to economically thicken wastewater resources in order to reduce holding tank capacity and optimize AD via 8%-10% solids
- Composition of organic matter contained in wastewater resources
- Utilizing proprietary biocatalysts to increase solids destruction and subsequent biomethane production by 25% while reducing BOD
- Utilizing state-of-the-art AD technology for retaining bacteria, ensuring adequate mixing, thermophilic digestion and biogas refining
- Utilizing thermal integration from power generation technologies such as high temperature fuel cells with CHP that can approach 90% efficiency in order to reduce internal energy costs, particularly for incorporation of thermophilic digesters
- The ability to utilize the nutrient rich effluent produced during AD as a value added fertigation stream for controlled environment agriculture (CEA) such as hydroponic greenhouses and new generation algal photobioreactors
- Grinding solids can increase surface area exposure and enhance solids destruction which increases biomethane production

Successful modeling and full-scale application of high rate wastewater processing has been accomplished for WWTFs and beer breweries ([Ramsey and Pullammanappallil 2005](#); [Lettinga et al 1999](#)). By Mar 2008, FuelCell Energy had contracted/installed five MCFC applications at wastewater treatment facilities in CA.

Table 20. Biomass Resources by Price: Quantities Assumed To Be Available in 2020 (EIA USDOE: Biomass for Electricity Generation)

Price (2000 Dollars per Million Btu)	Quantities Available	Agricultural Residues not including Animal Waste	Energy Crops	Forestry Residues	Urban Wood Waste/ Mill Residues	Total
5.00	Trillion Btu	2,335	1,501	2,034	1,230	7,100
	Million Dry Tons	136	87	118	72	413
	Million Wet Tons	194	124	169	103	590
	Equivalent Capacity (Gigawatts) ^a	32	21	28	17	98
2.50	Trillion Btu	1,147	254	34	493	1,928
	Million Dry Tons	67	15	2	29	113
	Million Wet Tons	96	21	3	41	161
	Equivalent Capacity (Gigawatts) ^a	16	3	0	7	26
1.25	Trillion Btu	0	0	0	234	234
	Million Dry Tons	0	0	0	14	14

	Million Wet Tons	0	0	0	20	20
	Equivalent Capacity (Gigawatts) ^a	0	0	0	3	3

^aAssuming biomass integrated gasification combined-cycle (BIGCC) technology. This is a hypothetical calculation based on the assumptions below and is not related to the capacity numbers reported in NEMS.

Energy Density

Biomethane can be higher in energy density and cleaner burning than natural gas which varies in energy density according to composition. In fact, biohythane, which is a hybrid fuel containing 7% biohydrogen gas and 93% biomethane gas (on a mass basis), can be utilized with current compressed natural gas (CNG) infrastructure. In volumetric form, biohythane consists of 20% biohydrogen and 80% biomethane. Biohythane is higher in energy density and is considerably cleaner burning than low grade natural gas.

In contrast to biohythane which consists of pure methane and hydrogen gas produced from biological resources such as biomass and organic waste, Hythane® is produced from natural gas and synthetic hydrogen production. The volumetric energy density of Hythane® is within 5% of methane. Hythane® reduces emissions of NO_x (the major contributor to photochemical smog) and other greenhouse gases by up to 50% in comparison with natural gas. Even greater reductions in emissions would be expected for combustion of biohythane.

Since the energy density for hydrogen gas (H₂) is 709 BTU/cu ft, and the energy density for methane (CH₄) is 1008 BTU/cu ft, the energy density for biohythane would be less than methane at 948 BTU/cu ft @ 60 °F [(0.20 cu ft_{H2}) x (709_{BTU/cu ft})] + [(0.80 cu ft_{CH4}) x (1,008_{BTU/cu ft})]. However, as pressure increases for compressed storage and use, energy density also increases proportionately for hythane. For example, at 5,000 psi pipeline pressure, hydrogen gas would contain 114,285 BTU/cu ft. Hence, biohythane would be equivalent to 380,264 BTU/cu ft which reflects a 6% increase in energy compared to biomethane.

Table 21. Storage Pressure - Density – Energy Content of Biogas (60% CH₄ + 39% CO₂), Methane (CH₄), Natural Gas and Hythane (80% CH₄ + 20% H₂ by volume) @ 60 °F

Compressibility		Density				Energy			
Pressure	Factor	Biogas	NG	CH₄	BioHythane	Biogas	NG	CH₄	BioHythane
psi		lb/cu ft				Btu/cu ft			
14.7 (atm)	1.0	0.0690	0.044 to 0.056	0.0423	0.0342	616	900 to 1,100	1,008	948
15	1.0	0.0704		0.0432		629		1,029	
20	1.0	0.0939		0.0575		839		1,372	
25	1.0	0.117		0.0719		1,049		1,715	
30	1.0	0.141		0.0863		1,258		2,058	
35	1.0	0.164		0.101		1,468		2,401	
40	1.0	0.188		0.115		1,678		2,744	
45	1.0	0.211		0.129		1,888		3,088	
50	1.0	0.235		0.144		2,098		3,431	
60	1.0	0.282		0.173		2,517		4,117	
70	1.0	0.329		0.201		2,937		4,803	

80	1.0	0.376		0.230		3,357		5,489	
90	1.0	0.423		0.259		3,776		6,176	
100	1.0	0.470		0.288		4,196		6,862	
125	1.0	0.587		0.360		5,245		8,577	
150	1.0	0.704		0.432		6,294		10,293	
175	1.0	0.822		0.504		7,343		12,008	
200	0.99	0.949		0.581		8,477		13,863	
250	0.98	1.19		0.732		10,672		17,452	
300	0.98	1.44		0.885		12,911		21,114	
350	0.97	1.69		1.04		15,141		24,760	
400	0.97	1.94		1.19		17,364		28,395	
450	0.96	2.21		1.36		19,773		32,335	
500	0.94	2.48		1.52		22,179		36,269	
600	0.93	3.02		1.85		26,976		44,114	
700	0.92	3.57		2.19		31,978		52,212	
800	0.91	4.13		2.53		36,891		60,327	
900	0.89	4.75		2.91		42,435		69,393	
1000	0.88	5.34		3.27		47,686		77,979	
1500	0.82	8.59		5.26		76,762		125,528	
2000	0.78	12.04		7.38		107,599		175,954	
2500	0.79	14.86		9.11		132,796		217,158	
3000	0.81	17.39		10.66		155,421		254,156	
3500	0.84	19.56		11.99		174,848		285,925	
4000	0.88	21.34		13.08		190,744		311,918	
4500	0.92	22.97		14.07		205,257		335,651	
5000	0.96	24.46		14.99		218,561		357,407	380,264

Analytical Methodology for Anaerobic Digestion of Animal Waste

[Chastain et al. \(1999\)](#) reports the biogas energy obtained per AU for fattened cattle, milk cows, swine and poultry calculated using Hill's biogas from manure equation (Hill, 1991; [Cuéllar and Webber, 2008](#)). In addition, the number of AUs in the US are listed in table 22 ([Kellog et al., 2000](#)).

Table 22. Annual energy available in the US from manure, sorted by animal category.

Animal type	Animal units (millions)	Biogas energy per animal unit/day (thousand BTU)	Biogas energy/year (trillion BTU)
Fattened Cattle	9.6	25.7	89.9
Milk cows	12.3	20.6	92.4
Other beef and dairy cattle	58.8	23.2	497
Swine	8.5	39.8	124
Poultry	6.1	56.0	125
Total			928

The number of animal units in the US and the energy produced per AU per day can be combined to find the total raw energy available on a daily and annual basis from manure-derived biogas (E_{biogas}) as also listed in table 22.

Potential for Increasing Production Efficiencies:

Innovative Technologies & Closed Loop Systems Architecture

As noted in table 22, animal manure can yield up to 928 trillion BTU of raw energy annually, or approximately 1 quad (quadrillion BTU). For reference, in 2005, the total US energy consumption was 100 quads (US DOE EIA, 2007), thus livestock manure can potentially be a renewable source for approximately 1% to as high as 6.5% of total annual energy consumption in a renewable and flexible biofuel (biogas) that can be refined, combusted, or reformed to hydrogen onsite to produce heat and electricity. Biomethane can also be transformed into CNG or hythane (hybrid fuel consisting of 7 w/w% hydrogen and 93 w/w% methane) for widespread use and reduction of GHGEs. Efficient animal diets, animal waste collection and state-of-the-art processing via high rate thermophilic anaerobic digesters could more than double conventional power production via high temperature fuel cells and distributive generated combined cooling heat and power (DG-CHP). Based on each AU producing 100 SCF per day of biogas at 80% methane, it is theoretically possible to produce 80,000 BTU per AU per day for cattle, e.g. 29 MBTU of biomethane per AU on an annual basis.

The energy from biogas can be converted to electricity with a typical efficiency of 34–40% for large turbines and with an efficiency of 25% for smaller generators (Nielson, 2002; Tafdrup, 1995). For high temperature fuel cells, electric efficiency can reach 47% for molten carbon technology, and close to 60% with addition of a rankine heat engine which converts exhaust heat to additional electricity.

For the following analysis a range of turbine efficiency from 25–40% was used, and total energy efficiency of 90% (47% electric efficiency and 43% heat capture for thermal integration) for a molten carbonate fuel cell. Equation (1) can be used with generation efficiencies to determine the amount of electricity possible from biogas, e_{biogas} . For this analysis the range of efficiencies used for the figures in table 23 are 25%, 40%, and 90%.

Equation 1: $e_{\text{biogas}} = E_{\text{biogas}} \times n$

e_{biogas} = the amount of electricity possible from biogas

E_{biogas} = the unconverted raw energy in the biogas (typically listed in BTUs)

n = the overall conversion efficiency of biogas to electricity

Including unit conversions, the total electricity in kWh that can be produced from biogas can be found with the following equation.

Equation 2: $e_{\text{biogas}}[\text{kWh}] = E_{\text{biogas}}[\text{BTU}] \times 0.00293 [\text{kWh/BTU}] \times n$

Equation (2) was evaluated for each animal type for the lower and upper values of the efficiency range. The results of this calculation are summarized in the following table.

Table 23. Electricity possible from biogas for each animal type.

Animal type	Electricity and CHP possible from biogas (billion kWh)		
	Low ($\eta = 25\%$)	Medium ($\eta = 40\%$)	High ($\eta = 90\%$ Total Energy Efficiency via 47% Electric & 43% Combined Heat & Cooling)
Fattened cattle	6.6	10.5	23.625
Milk cows	6.8	10.8	24.3
Other beef and dairy cattle	36.4	58.2	130.95
Swine	9.1	14.5	32.625
Poultry	9.2	14.7	33.075
Total	68.0	108.8	244.575

The US consumes 3.8 trillion kWh of electricity annually (US DOE EIA, 2007). Thus the 68.0 billion kWh possible from biogas at a low-end efficiency of 25% represents 1.8% of the total annual electricity consumption. At the medium-end conversion efficiency of 40%, the 108.8 billion kWh from manure represents 2.9% of the total electricity consumed in the country. At the high-end conversion efficiency for DG-CHP produced by high temperature fuel cells, the 244.575 billion kWh from manure represents 6.52% of the total electricity and process steam consumed in the US.

GHGEs from the burning of biogas also need to be considered. The method of Murphy et al (2004) was used to determine the emissions that would result from the combustion of biogas with a methane fraction of 60–70% and CO₂ content of 30%–40%, which is the typical composition of biogas (Balsam, 2002; Murphy et al., 2004; Lansing et al., 2008). The emissions are determined using the stoichiometric amount of CO₂ produced by complete combustion of the methane molefraction of biogas plus the balance of CO₂ in the biogas that is assumed, for this analysis, to pass through the combustion process unchanged. The emission factor is then combined with the energy content of biogas and the efficiency of its conversion to electricity to determine the CO₂ released per kilowatt hour of electricity produced.

The combustible component of biogas is methane (CH₄). Equation (3) is the methane combustion reaction for stoichiometric conditions.



This equation reveals that the combustion of one mole of methane produces one mole of carbon dioxide. Changing this conversion to a mass basis using molecular weights shows that 16 g of methane produce 44 g of CO₂. In other words, 2.75 kg of CO₂ is produced from the complete

combustion of 1 kg of methane. At standard conditions, which nominally prevail for this analysis, methane and CO₂ have densities of $\rho_{\text{CH}_4} = 0.65$ and $\rho_{\text{CO}_2} = 1.80 \text{ kg m}^{-3}$, respectively. The total amount of CO₂ produced from the combustion of one cubic meter of biogas is shown in equation (4) below, where $x_{\% \text{CH}_4}$ is the percent content of methane in the biogas by volume with the balance of gas comprised of CO₂.

$$\text{Equation 4: } \text{kg}_{\text{CO}_2 \text{ total}} = 1 \text{ m}^3_{\text{biogas}} (x_{\% \text{CH}_4} \times \rho_{\text{CH}_4} \times 2.75 + \rho_{\text{CO}_2} [1 - x_{\% \text{CH}_4}])$$

ρ_{CH_4} = at ambient temperature density of methane in biogas = .65

ρ_{CO_2} = at ambient temperature density of carbon dioxide in biogas = 1.8 kg m⁻³

$x_{\% \text{CH}_4}$ = the per cent content of methane in the biogas by volume with the balance of gas comprised of CO₂.

Equation (4) reveals that the total carbon dioxide emissions from the combustion of one meter cubed of biogas is the sum of the carbon dioxide content in the biogas and the amount of carbon dioxide resulting from the combustion of methane.

Notably, stoichiometrically combusting one cubic meter of biogas yields 1.8 kg of CO₂ after combustion no matter what portion is comprised of methane. From these results it can be concluded that, theoretically, the emissions of CO₂ from the combustion of biogas are constant in spite of changes in its composition. The energy content of the gas is the only factor that varies with methane content. That is, even though CO₂ emissions from biogas combustion are dependent only on the volume of biogas/biomethane combusted, the amount of useful energy that can be extracted depends on the methane mole fraction of the fuel.

The higher heating value (HHV) of pure methane is 55.6 MJ kg⁻¹, which yields a volumetric energy density of 36 MJ m⁻³ at standard conditions. The energy density, $E_{\% \text{CH}_4}$, can be linearly scaled down to diluted concentrations in biogas (for example, biogas with 55% methane content has about 20 MJ m⁻³, which roughly agrees with the values reported by Murphy et al (2002). The values of energy density and CO₂ emissions (if combusted) for a variety of methane molefractions (from 50 to 100%) are plotted in figure 8.

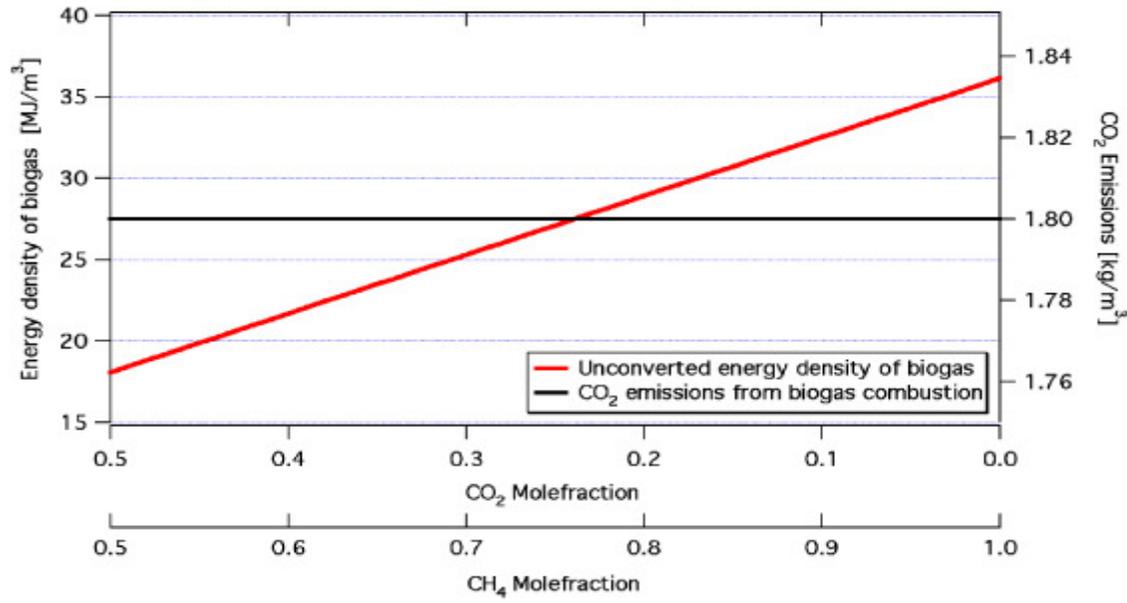


Figure 8. Plot of the energy density of biogas and resulting carbon dioxide emissions from combustion versus the composition of the biogas.

These values can be converted to kilowatt hours by using the conversion factor of 3.6 million joules per kilowatt hour. To determine the amount of electricity that can be generated from this energy density an efficiency factor (η) of 25–40% was again used to determine that one cubic meter of biogas with 60% methane content produces 1.51 kWh of electricity when converted at 25% efficiency, while a cubic meter of biogas with 70% methane content that is converted at 40% efficiency produces 2.81 kWh of electricity. A cubic meter of biomethane

This energy content information can be combined with the emissions results to find the carbon dioxide produced per kilowatt hour of electricity generated, which is a function both of the methane molefraction and the conversion efficiency. Equation (5) was used to find the emissions factors. In this equation, $E_{\%CH_4}$ is the energy density of biogas as a function of methane molefraction and expressed in kWh m⁻³ of biogas.

$$\text{Equation 5: } \zeta_{CO_2} = 1 \text{ m}^3_{\text{biogas}} (x_{\%CH_4} p_{CH_4} 2.75 + p_{CO_2} [1 - x_{\%CH_4}]) / E_{\%CH_4} \eta$$

ζ_{CO_2} = kg of CO₂ per kWh of electricity

p_{CH_4} = at ambient temperature density of methane in biogas = .65

p_{CO_2} = at ambient temperature density of carbon dioxide in biogas = 1.8 kg m⁻³

$x_{\%CH_4}$ = the per cent content of methane in the biogas by volume with the balance of gas comprised of CO₂.

$E_{\%CH_4}$ = the energy density of biogas as a function of methane molefraction and expressed in kWh m⁻³ of biogas

The resulting emissions factors (ζ_{CO_2} , in kg of CO₂ per kWh of electricity) are plotted in figure 9, showing that CO₂ emissions per kilowatt hour are lowest for efficient combustion of biogas

streams that have relatively higher methane content. Biogas containing 60% methane and combusted at 25% efficiency emit 1.13 kg CO₂ per kWh of electricity whereas 70% methane combusted at 40% efficiency emits 0.64 kg CO₂ per kWh of electricity generated. By comparison, pure methane emits approximately 0.52 kg of CO₂ per kWh of electricity under typical combustion conditions ([US EPA](#)), which agrees with the values on the plot.

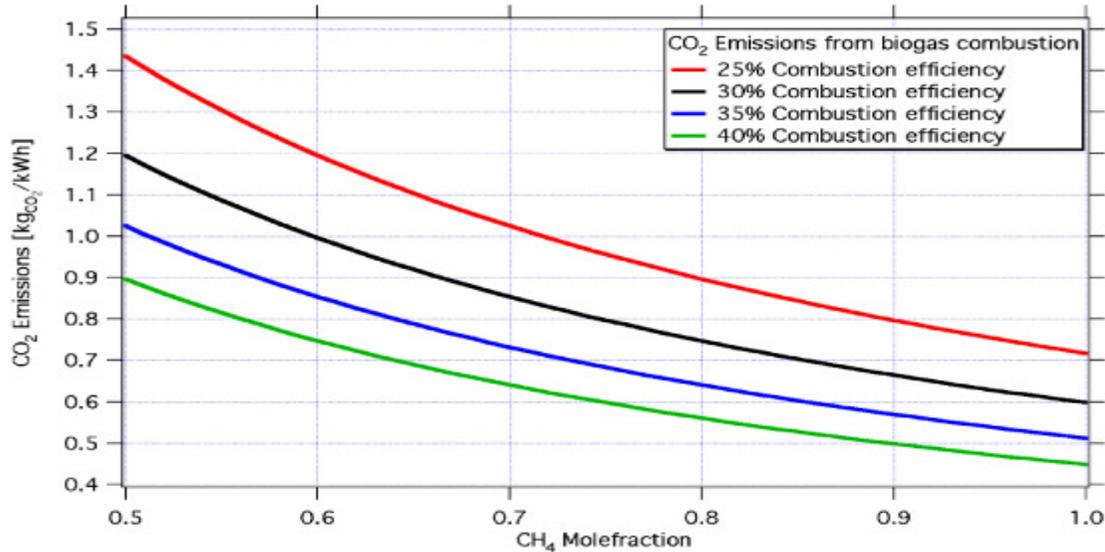


Figure 9. Carbon dioxide emissions from biogas electricity generation depending on the methane molefraction and combustion efficiency.

These emission factors can now be used to determine the annual emissions from biogas (y_{total}) when it is used for power generation. Equation (6) was used for this conversion, which produced the results listed in Table 24.

Equation 6: $y_{total} = e_{biogas} \zeta_{CO2}$

y_{total} = annual emissions from biogas

e_{biogas} = the amount of electricity possible from biogas

ζ_{CO2} = kg of CO₂ per kWh of electricity

Table 24. Total annual emissions of carbon dioxide from electricity generation using biogas combustion for the low- and high-efficiency cases with typical methane molefractions of 60%, 70% and goal of 100% biomethane via refining biogas and recycling CO₂.

	CO ₂ emissions from biogas-fired electricity generation (million metric tons)		
Animal type	60% methane, 25% efficiency	70% methane, 40% efficiency	100% methane, 90% total energy efficiency with CO ₂ recycled
Fattened cattle	7.4	6.8	0

	CO₂ emissions from biogas-fired electricity generation (million metric tons)		
Animal type	60% methane, 25% efficiency	70% methane, 40% efficiency	100% methane, 90% total energy efficiency with CO ₂ recycled
Milk cows	7.7	6.9	0
Other beef and dairy cattle	41.2	37.3	0
Swine	10.3	9.3	0
Poultry	10.4	9.4	0
Total	77.0	69.6	0

In total, the annual emissions from biogas combustion vary from 69.6 to 77 million metric tons of CO₂. Table 24 lists CO₂ emissions from each animal type and the total emissions from all animals.” (Cuéllar and Webber, 2008)

However, for integrated operations which refine biogas to pure biomethane and recycle CO₂ along with nutrient-rich effluents to produce closed loop biomass, GHGEs and pollution from nutrient run-off are essentially eliminated via comprehensive nutrient-energy management.

Organic Waste Processing & Biogas Production

Anaerobic digestion converts organic waste into renewable biogas, organic compost, and nutrient rich biological effluents for use as value added fertigation streams for enhancing crop production via organic fertilizers. The biogas is rich in biomethane and carbon dioxide. Biomethane can displace natural gas (which consists primarily of methane) as a renewable energy resource. It can also be utilized to produce biohythane, a hybrid fuel consisting of 93% biomethane and 7% biohydrogen by mass (20% hydrogen by volume). Biohythane substantially reduces GHGEs by utilizing renewable fuels. Carbon dioxide can then be utilized as a value added nutrient for biomass production via photosynthesis. Once conversion efficiencies improve, CO₂ can also be converted into ethanol via the r-WGS reaction and hydrogenation as described above. In addition, biomethane can be utilized as a renewable feed for high temperature fuel cells. This essentially allows for solar powered fuel cells which provide distributive generated combined heat and power (DG-CHP) and cogeneration of hydrogen for closed loop systems.

Anaerobic digestion is a series of microbial processes in which biodegradable material is decomposed in the absence of oxygen. It is widely used to treat organic waste and wastewater sludge because it converts organic matter into inorganic nutrients which plant life can utilize via photosynthetic growth processes. Anaerobic digestion conserves mineral nutrients such as N-P-K and micronutrients for use as organic fertilizers in order to replenish soil organic matter. Efficient animal waste collection and processing can reduce urea hydrolysis, ammonia volatilization, nitrous oxide and methane emissions which contribute to global warming.

Anaerobic digestion is five to ten times more efficient than aerobic processing which is currently utilized in the sewage processing and municipal wastewater industry. As part of an integrated waste management system, anaerobic digestion reduces greenhouse gases (including CO₂, nitrous oxides and methane) and pungent odors emitted by CAFOs, food processors, landfills and sewage treatment centers. Biogas is suitable for energy production and displacing fossil fuels such as natural gas. Nutrient-rich biological effluents and solids remaining after digestion, including lignin, can reduce synthetic fertilizer purchases by as much as 80% for integrated operations and closed loop biomass production.

The quantity and quality of biogas produced depends on the composition of the organic substrates. Ideal substrates contain 15:1 to 30:1 carbon to nitrogen ratios. On average, animal waste for cattle contains a 25:1 ratio. The quality of animal waste varies depending on type of animal and quality of feed ration. Protein/nitrogen content in swine and poultry waste is considerably higher than it is for cattle. Optimal biogas production from animal waste is achieved through feeding balanced rations and efficient animal waste collection.

The anaerobic digestion process begins with pretreatment and bacterial hydrolysis of the input materials (substrates) in order to break down insoluble organic polymers such as carbohydrates and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide (CO₂), hydrogen (H₂), ammonia (NH₃), and organic acids. Acetogenic bacteria subsequently convert organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Methanogens then convert these products to biomethane (CH₄) and carbon dioxide. Biocatalysts can increase solids destruction and thus increase methane production by 25% for conventional digesters.

High rate mesophilic anaerobic digesters (such as Induced Blanket Reactor or IBR technology) can process animal waste in as little as 3-5 days, providing 45% solids destruction with an 8-10% loading rate for solids. This results in producing 60-87 SCF per AU (1000 lbs of animal) per day at 60-70% methane and 30-40% CO₂ concentrations. The IBR technology utilizes an auger and septum along with columnar design for digester tanks to prevent bacteria from exiting with the effluent, and thus achieve high rate processing. IBR digesters utilize an *in situ* sludge/sand removal process. The 12' wide x 30' tall digesters are housed in insulated buildings in temperate climates to reduce heating costs.

In contrast to IBR technology, the high solids anaerobic digester (HSAD) technology utilizes thermophilic processing and can process 20-55% solids loading rates. Hydraulic retention time (HRT) for the HSAD technology is 14-21 days for conversion of a variety of substrates including animal waste, food processing waste, paper, packaging waste, municipal solid waste and sewage sludge. Thermophilic, as opposed to mesophilic processing, can decrease hydraulic retention time (HRT) by as much as 20% while increasing biomethane production. Thermophilic processing also kills over 99.9% of pathogens in organic waste. Substrates are preheated to 55 °C (135 °F) prior to entering the digester. The HSAD process was developed over a ten year period by NREL utilizing selective microbial populations without requiring the use of biocatalysts. The increase in organic carbon conversion and solids destruction, from 45% to 65%, results in proportionately increasing efficiency of biogas production. Organic waste pretreatment and biocatalysts may increase solids destruction.

Between 60-80% methane and 20-40% CO₂ is produced by HSAD technology ([North Carolina State University, 2005](#)). Although the precise composition of a biogas depends on the waste feedstock, humidity and other process parameters, methane accounts for about 60 to 80% of the biogas volume and carbon dioxide comprises the balance (20 to 40%).

The volume of biogas generated from an HSAD reactor depends on the proportion of degradable materials (volatile solids) present in the organic waste, which are the "food" for the anaerobic microorganisms that thrive in the HSAD bioreactor. Since the degradable fraction varies from one material to another, feedstocks introduced into an HSAD reactor decompose in different proportions. For example, the proportion of organics that degrades in food waste is generally larger than that in yard waste. Still, HSAD converts up to 90% of the available organic carbon into biogas, and destroys up to 65% of solids. The remaining solids are converted to mineral-rich organic compost relatively high in N-P-K and micronutrients.

Under normal conditions (that is, one atmosphere at 131° F or 55° C), the typical yield from an HSAD bioreactor is 6 decatherms (6.3 million kilojoules) per ton of organic waste. Therefore, a 100 ton (90,718 kilogram) per day plant produces 600 Dth (633 million kilojoules or 600 MBTU) per day and around 1 million standard cubic feet (SCF) of biogas containing 60% methane. This is equivalent to producing 28,316 cubic meters of biogas. At 80% methane, the equivalent of 800 MBTU per day would be produced.

There are several ways to use the biogas, including powering an internal combustion engine to generate electricity. Biogas can also be combusted directly for heating, industrial boilers or kilns, or used to power fuel cells and gas turbines. A 100 ton per day HSAD plant processing waste feedstocks such as food waste (or the organic fraction of municipal solid waste) will have an electrical power generation capacity of 2.4 to 3.0 MW. For high temperature molten carbonate fuel cell (MCFC) applications, 600 MBTU per day would provide 3.47 MW and 4.65 MBTU/hr for thermal integration via an exhaust temperature of 750 °F. 800 MBTU per day would provide 4.62 MW and 6.20 MBTU/hr for thermal integration.

For CAFOs, 100 SCF/day/AU is possible for HSAD reactors via integration of efficient animal waste collection with high solids destruction and mixing animal waste with substrates high in fatty acids and carbohydrates in order to boost methane production. This is achieved with state-of-the-art thermophilic HSAD technology which optimizes the microbial environment. Based on the increase in carbon conversion and solids destruction, harvesting 100 SCF/day per AU could produce 80,000 BTU/AU/Day (29 MBTU/yr/AU) for integrated operations. This could increase biogas production by over 5 fold in comparison with conventional digesters, and over 3 fold in comparison with IBR digester technologies. Conventional & IBR mesophilic digesters produce 55-70% methane and harvest 50-70 SCF/day per AU (7-10 MBTU/yr/AU).

In addition to increasing biogas production, efficient animal waste collection reduces urea hydrolysis/ammonia volatilization, and subsequent odors. For integrated operations, waste heat from biorefining (such as high temperature molten carbonate fuel cells, etc.) can be utilized via underground ducts/pipes to reduce ground freezing and enhance animal waste collection. This would simultaneously allow for reducing temperatures of exhaust gas from fuel cells for use as

CO₂ enriched space heat for CEA applications. In addition, heat exchangers utilized for cooling fermentors could be utilized to prevent animal water from freezing for integrated operations.

Similar to IBR technology, the HSAD technology has a relatively small footprint which is enhanced by high solids loading rates, agitators, and rectangular design. The HSAD technology requires only 10-15% of the energy that it produces to heat the digester and provide the necessary power required for operation. In addition to high quality biogas, the closed HSAD system produces organic compost rich in nitrogen and phosphorous along with value added liquid fertilizers which are free of pathogens and weed seeds.

Prior to pretreatment of organic waste, macerators can be used to reduce particle size to 5-10 mm. This enhances enzymatic and microbial processing of organic waste substrates. Pretreatment technologies such as force pulse, ultrasonic cavitation, and electroporation can enhance solids destruction which increases efficiency and volume of biogas production for conventional AD technologies. Uniform reduction of particle size via macerators, innovative pretreatment, and biocatalysts may allow for reduction of the 16-30 day hydraulic retention time (HRT) currently required for the HSAD technology. Upon completion of the digestion process, screw presses are utilized to separate solids (organic compost) from biological effluents. Biogas refining technology and microbes can be utilized to break down H₂S and separate CO₂ from the biomethane.

Optimizing Carbon:Nitrogen Ratio for Increasing CH₄ Concentrations

Though methane concentrations in biogas produced from cattle manure typically range from 55-65% depending on diets and efficiency of anaerobic digestion, methane concentration can be increased by adding fatty acids and mixed substrates with relatively little nutritional or feed value for animals. Different plant wastes containing digestible volatile solids (VS) have been tested in admixture with animal manure for their effect in increasing methane output in anaerobic digestion. For example, a mixture of animal waste, algae and water hyacinth in equal proportions provided a carbon:nitrogen ratio of 29.5 and produced 79% methane in biogas for a mesophilic digester maintained at 35 °C without regulating pH over a 15 day period.

This was accomplished by increasing the availability of hydrogen donors contained in easily-digestible volatile solids. Volatile solids are the portion of biomass that is combustible (e.g. total solids in the slurry minus ash minerals which remain after combustion). Increasing concentration of volatile solids to achieve a 30:1 ratio of carbon to nitrogen results in converting more carboxylated intermediates to methane rather than CO₂ (Ghose and Mukhopadhyay, 1976; Barkar, 1956). Additionally, increasing efficiency of anaerobic digestion results in increasing methane concentration ([Ghose et al., 1979](#)). Though the data collected for this research project was based on utilizing mesophilic bacteria, similar increases in efficiency of anaerobic digestion would be expected using thermophilic bacteria at higher temperature ranges.

Table 25. Variation in production and composition of biogas as a function of C/N ratio at different temperatures during a 15 day period.

Temp. (°C)	Parameter	Carbon:Nitrogen Ratio						
		10	16	19.5	29.5	40	50	60

35	Biogas	5.0	5.1	5.3	6.0	4.4	4.0	3.8
	CH₄	71.0	71.8	72.0	78.0	69.5	67.5	66.0
40	Biogas	4.1	4.2	4.3	5.4	4.6	4.4	4.0
	CH₄	63.5	65.5	68.0	72.0	65.0	63.0	62.0
50	Biogas	3.8	4.0	4.1	4.7	4.0	3.7	3.3
	CH₄	59.5	63.0	68.2	70.7	64.0	63.0	61.5

(Table adapted from [Ghose et al., 1979](#))

The IBR digester technology has achieved as high as 70% methane with a 4 day HRT with 8-10% TS using only dairy waste substrate. Supplementing dairy waste with equal portions of algae and water hyacinth should produce similar methane concentrations for both the IBR and thermophilic HSAD technologies. Most vegetable matter has a lower carbon to nitrogen ratio than animal waste, so nitrogen rich feedstocks such as vegetable matter must be added to enhance biogas production via anaerobic digestion. However, efficient collection of animal urine with manure could substantially increase the urea nitrogen level contained in animal waste substrates.

Table 26. Analysis of different organic residues.

Parameter	Animal Waste	Water Hyacinth	Algae	Sugarcane Bagasse	Rice Husks	Corn Stover
VS (% of TS)	80.0	78.0	78.0	70.0	70.0	
Nitrogen “	1.9	3.8	6.65	0.45	0.5	
Carbon “	37.0	48.0	46.5	43.5	39.5	
C:N Ratio	19.5	12.6	7.0	96.6	79.0	

(Table adapted from [Ghose et al., 1979](#))

It is interesting to note that algal biomass is lignin-free and water hyacinth contains less lignin than crop residues such as bagasse, rice husk and corn stover. Corn stover and cereal grain straw are expected to have similar values as those listed for sugar cane bagasse and rice husks. Both algae and water hyacinth are aqueous plant species vs. terrestrial crop residues which are substantially higher in lignin and cellulose. Since lignin is not readily digested by anaerobic digestion, the lower volume of lignin contained algae and water hyacinth increases the volume of volatile solids which subsequently increases biogas production and methane concentration.

Table 27. Availability of biogas from various organic residues.

Biomass Resource	Initial		% VS Consumed	Biogas (l/kgTS)	CH₄	
	TS	VS			(%)	(l/kgVS)
Animal Waste	40	31	42	2.8	59	1.7
	60	47	38	4.4	60	2.64
	100	79	29	6.5	62	4.03
Water Hyacinth	40	33	51	4.0	68	3.72
	60	48	44	6.3	68	4.28
	100	83	30	9.9	68	6.73
Algae	40	32	52	4.1	70	2.90
	60	50	47	7.2	74	3.36
	100	80	36	10.8	73	7.88

Sugarcane Bagasse	40	32	41	2.2	50	1.10
	60	47	36	3.9	50	1.96
	100	79	25	5.7	53	3.04
Rice Husks	40	31	40	2.0	48	1.00
	60	47	35	3.4	48	1.38
	100	75	25	5.4	49	2.69

(Table adapted from [Ghose et al., 1979](#))

The above table illustrates biogas production as a function of the solids loading rate for anaerobic digestion during a 15 day period. Loading rate for VS has a substantial effect on consumption (solids destruction) and subsequent volume of biogas produced:

- As VS loading rate increases, percent VS consumption rate decreases, while total VS consumption and daily total gas production rate increase linearly.
- Percent VS consumption and quantity of biogas produced are both higher from algae and water hyacinth than from animal waste.
- The gas production and VS consumption from crop residues such as rice husk and bagasse are both lower than that produced from animal waste. ([Ghose et al., 1979](#))

Weight for weight, fresh vegetable and lignocellulosic biomass (including algae and water hyacinth) produces about eight times more biogas as manure biomass, so the quantity required as an anaerobic digester feedstock is much smaller for the same volume of biogas produced. By mixing fibrous biomass (highly indigestible lignocellulosic feedstocks and food processing waste rich in lipids which have marginal nutritional value for most animals), methane concentration in biogas can be increased to 80% without utilizing food crops or high quality biofuel feedstocks. Some studies reveal that utilizing the same biomass feedstocks, anaerobic digestion can produce more energy than that which results from production of biodiesel via conventional FAME processing ([Gunaseelan, 2008](#)). Production costs for anaerobic digestion are also considerably less than most FAME conversion processes. Hence, algal biomass rich in carbohydrates and lipids appears to be an ideal feedstock for mixing with animal waste.

Forced Pulse, Ultrasonification & Electroporation Pretreatment

Regarding pretreatment of organic waste, pulse and force pulse consist of an electric current which is released in extremely short bursts. Steady accumulation of energy followed by its rapid release can result in the delivery of a larger amount of instantaneous power over a shorter period of time (although the total energy is the same). Energy is typically stored within electrostatic fields (capacitors), magnetic fields (inductor), as mechanical energy (using large flywheels connected to special purpose high current alternators), or as chemical energy (high-current lead-acid batteries, or explosives).

For example, high temperature fuel cells can provide the electric current which is stored in a capacitor. By releasing the stored energy over a very short interval, peak power delivered to a load can be increased exponentially. For example, if one joule of energy is stored within a capacitor and then evenly released to a load over one second, the peak power delivered to the load would be 1 watt. However, if that stored energy was released within one microsecond, the peak power would be one megawatt, a million times greater.

Such a pulse power is characterized as a powerful shockwave which is transmitted faster than acoustic velocity in gas phase such as air. It can also induce a stable arc discharge as a plasma phase between two electrodes by an instant discharge of energy in water. The arc discharge is generated using high pulse power in water which produces a shockwave characterized by intense UV (ultraviolet) radiation, strong electric field, and various radicals. 50% of the applied energy is converted to the shockwave which induces an explosion. This activates the evaporation and the decomposition of liquid during the electric discharge in liquid phase such as water. This shockwave destroys solids of organic waste biomass.

An electric current of 10 to 100A is generated in applying the voltage of 10 to 100V, and the frequency of pulse is from 60 to 120Hz. Instant temperature change occurs when pulse power is generated which makes the liquid phase expand and re-condense. A pressure difference occurs and pulse power is generated in the same space. By such an effect, the organic wastes contacted with pulse power change particles, cell walls, organic polymers, and the electric charge among the particles. The volatile solid matters of the particulate type are hydrolyzed to soluble substances such as glucoses, fat, proteins, and fatty acids which microbes can more efficiently digest.

Ultrasonic cavitation may be utilized to increase surface area of grain, biomass, and organic waste in order to enhance efficiency of enzymatic and microbial processing. This process has been shown to be effective with corn starch and switchgrass feedstocks. For treatment of corn slurries, particle size is decreased by nearly 20-fold following ultrasonic treatment at high power settings. In bench tests, the glucose release rate from sonicated samples increased by as much as 3-fold and enhanced enzymatic processing. The efficiency of ultrasound exceeded 100% in terms of energy gain from the sugar released over the ultrasonic energy supplied. In addition, ultrasonic energy gelatinizes starch at relatively low temperatures (30-50 °C), much faster compared to heating. It is believed that this also promoted hydrolysis of the polysaccharides (Grewell, 2008; [Khanal et al., 2007](#)). For switchgrass, sequential ammonia steeping-ultrasonic pretreatment released about 10% more fermentable sugars than did ammonia steeping alone. Similar results may be achieved for treating corn stover. However, in regards to lignocellulosic biomass, the energy balance for utilizing ultrasonics is currently much more favorable for starch feedstocks ([Montalbo-Lomboy, et al., 2007](#)).

[OptiSwitch Technology Corp.](#), a high-performance semiconductor device, module and system research and development company has developed a new process that increases ethanol yields from corn by 5 percent or more via electroporation. The project was funded with \$10 million contracted from the U.S. Department of Defense. The research was conducted and evaluated at the National Corn-to-Ethanol Research Center in Edwardsville, IL ([Austin, 2008](#)).

Optimizing Processing of Organic Waste via Methane Production

There are two basic types of organic decomposition that can occur via fermentation: aerobic (in the presence of oxygen), and anaerobic (in the absence of oxygen) decomposition. All organic material, both animal and vegetable can be broken down by these two processes, but the products of decomposition will be quite different in the two cases. Aerobic decomposition (fermentation) will produce carbon dioxide, ammonia and some other gases in small quantities, heat in large quantities and a final product that can be used as a fertilizer. Anaerobic decomposition will

produce methane, carbon dioxide, some hydrogen and other gases in traces, very little heat and a final product with a higher nitrogen content than is produced by aerobic fermentation. Anaerobic decomposition is a two-stage process as specific bacteria feed on certain organic materials. In the first stage, acidic bacteria dismantle the complex organic molecules into peptides, glycerol, alcohol and the simpler sugars. When these compounds have been produced in sufficient quantities, a second type of bacteria starts to convert these simpler compounds into methane. These methane producing bacteria are particularly influenced by the ambient conditions, which can slow or halt the process completely if they do not lie within a fairly narrow band.

Acidity

Anaerobic digestion will occur best within a pH range of 6.8 to 8.0. More acidic or basic mixtures will ferment at a lower speed. The introduction of raw material will often lower the pH (make the mixture more acidic). Digestion will stop or slow dramatically until the bacteria have absorbed the acids. A high pH will encourage the production of acidic carbon dioxide to neutralise the mixture again.

Carbon:Nitrogen Ratio: 30:1

Temperature

Anaerobic breakdown of waste occurs at temperatures lying between 0°C and 69°C, but the action of the digesting bacteria will decrease sharply below 16°C. Production of gas is most rapid between 29°C and 41°C or between 49°C and 60°C. This is due to the fact that two different types of bacteria multiply best in these two different ranges, but the high temperature bacteria are much more sensitive to ambient influences. A temperature between 32°C and 35°C has proven most efficient for stable and continuous production of methane. Biogas produced outside this range will have a higher percentage of carbon dioxide and other gases than within this range.

Percentage of Solids

Anaerobic digestion of organics will proceed best if the input material consists of roughly 8 % solids. In the case of fresh cow manure, this is the equivalent of dilution with roughly an equal quantity of water.

Basic Design

The central part of an anaerobic biogas plant is an enclosed tank known as the digester. This is an airtight tank filled with the organic waste, and which can be emptied of digested slurry with some means of catching the produced gas. Design differences mainly depend on the type of organic waste to be used as raw material, the temperatures to be used in digestion and the materials available for construction. A simple reactor design is to gravity feed the underground tank, thus reducing energy intensive pumping, and allow the digested slurry to overflow the tank. This has the advantage of being able to consume more solid matter as well, such as chopped vegetable waste, which would block a pump very quickly. This provides extra carbon to the system and raises the efficiency. Cow manure is very nitrogen rich and is improved by the addition of vegetable matter.

Continuous Feeding of Liquids

The complete anaerobic digestion of cow manure takes about 8 weeks at normally warm temperatures. One third of the total biogas will be produced in the first week, another quarter in the second week and the remainder of the biogas production will be spread over the remaining 6 weeks. However, high rate digesters ([induced blanket reactors produced by Andigen](#)) have been designed to reduce hydraulic retention time (HRT) to less than 4 days for processing dairy waste to biogas. The biogas contains as much as 65%-70% methane via mesophilic digesters operating at 8%-10% loading rate for solids. The solids destruction rate is 45%.

Another high rate anaerobic digester has been developed by NREL over a ten year period. Unlike Andigen technology, it utilizes a 20-45% solids loading rate. Up to 65% of solids are converted to biogas and nutrient-rich effluents with a 16-20 day HRT. In comparison with Andigen's IBR technology, the longer HRT of the HSAD technology is partially offset by the higher solids destruction rate and the wide variety of substrates processed which results in increasing methane production. The closed, odorless system converts up to 85% of the organic carbon in solid organic waste material into biogas. The thermophilic system destroys over 99% of pathogens. Unlike Andigen technology, NREL's technology which is licensed by [Orbit Energy](#) is capable of processing animal hair and offal. High solids organic wastes processed include paper and packaging wastes, food processing wastes, agricultural wastes, sewage and industrial sludges, yard or green wastes, and municipal solid waste. These high solids waste feedstocks are best suited for the HSAD technology and generally unacceptable for other alternative energy technologies. HSAD utilizes standardized equipment from the chemical processing industry to handle and process organic solid wastes in the HSAD reactor. The HSAD uses specially selected bacterium operating at around 55 °C. The reactor requires only 10-15% of the energy produced for operation of digesters and biogas refining. Implementing innovative collection, management and economic pretreatment of substrates may allow for reducing energy consumed to less than 10% of total energy produced for HSAD applications. The effluent from the bioreactor produces two products: a moist, compost material enriched in valuable elements like nitrogen and phosphorus, and a liquid fertilizer. The HSAD process is a continuous unit operation that can be readily integrated into existing industrial plants and municipal solid waste sorting facilities. The HSAD system is almost completely automated, requiring minimal attention ([HSAD Brochure, Orbit Energy](#)).

Gas production can be accelerated and made more consistent by continuously feeding the digester with small amounts of waste daily. This will also preserve the nitrogen level in the slurry for use by microbes and also allow for using nutrient-rich biological effluents as value added organic fertigation streams for subsurface drip fertigation and controlled environment agriculture.

If such a continuous feeding system is used, then it is essential to ensure that the digester is large enough to contain all the material that will be fed through in a whole digestion cycle. One solution is to use a double digester, consuming the waste in two stages, with the main part of the biogas (methane) being produced in the first stage and the second stage finishing the digestion at a slower rate, but still producing another 20% or so of the total biogas.

Batch Feeding of Solids

There are biogas systems designed to digest solid vegetable waste alone. Since plant solids will not flow through pipes, this type of digester is best used as a single batch digester. The tank is opened, old slurry is removed for use as fertilizer and the new charge is added. The tank is then resealed and ready for operation.

Dependent on the waste material and operating temperature, a batch digester will start producing biogas after two to four weeks, slowly increase in production then drop off after three or four months. Batch digesters are therefore best operated in groups, so that at least one is always producing useful quantities of gas.

Most vegetable matter has a much higher carbon - nitrogen ratio than animal waste has, so some nitrogen producers (preferably organic) must generally be added to the vegetable matter, especially when batch digestion is used. Weight for weight, however, vegetable matter produces about eight times as much biogas as manure, so the quantity required is much smaller for the same biogas production. A mixture of animal waste and vegetable matter (such as food processing waste) is ideal. This allows for increasing methane concentration in biogas.

Stirring & Agitation

Some method of stirring the slurry in a digester is always advantageous, if not essential. If not stirred, the slurry will tend to settle out and form a hard scum on the surface, which will prevent release of the biogas.

This problem is much greater with vegetable waste than with manure, which will tend to remain in suspension and have better contact with the bacteria as a result. Continuous feeding causes less problems in this direction, since the new charge will break up the surface and provide a rudimentary stirring action. If some form of heating is needed for the digester, as is generally the case in temperate climates, this will also provide some circulatory action, which will tend to stir the contents.

Temperature Control

In hot regions it is relatively easy to simply shade the digester to keep it in the ideal range of temperature, but cold climates present more of a challenge.

The first action is, naturally, to insulate the digester with straw or wood shavings. A layer about 50 - 100 cm thick, coated with a waterproof covering is a good start. If this still proves to be insufficient in winter, then heating coils may have to be added to the biogas digester.

It is relatively simple to keep the digester at the ideal temperature if hot water, regulated with a thermostat, is circulated through the system. Usually it is sufficient to circulate the heating for a couple of hours in the morning and again in the evening. Naturally, the biogas produced by the digester can be used for this purpose. The small quantity of gas "wasted" on heating the digester will be more than compensated for by the greatly increased biogas production.

Biogas Collection

The biogas in an anaerobic digester is collected in an inverted drum. The walls of the drum extend down into the slurry to provide a seal. The drum is free to move to accommodate more or

less gas as needed. The weight of the drum provides the pressure on the gas system to create flow.

The biogas flows through a small hole in the roof of the drum. A non-return valve here is a valuable investment to prevent air being drawn into the digester, which would destroy the activity of the bacteria and provide a potentially explosive mixture inside the drum. Larger plants may need counterweights of some sort to ensure that the pressure in the system is correct. The drum must obviously be slightly smaller than the tank, but the difference should be as small as possible to prevent loss of gas and tipping of the drum.

Installing Above or Below Ground

Biogas plants constructed above ground must be made of steel to withstand the pressure within, and it is generally simpler and cheaper to build the digester below ground. This also makes gravity feed of the system much simpler. Maintenance is, however, much simpler for systems built above ground and a black coating will help provide some solar heating.

This should make it clear that biogas is not just a dream, but a practical application and use of a waste product. India already has around 3000 biogas plants of varying sizes.

The near half billion cattle, pigs and chickens in the US produce over two billion tons of manure every year, an incredible amount. This can be seen as a valuable natural resource capable of producing combustible gas that would reduce consumption of natural gas and provide a fertilizer more valuable than the raw manure.

Monitoring Biogas Quality

The matter of [measurements in biogas](#) must also be considered. The [carbon dioxide](#) and methane contained in biogas can best be measured with infrared technology using [infrared sensors](#). The gas produced and the slurry being fermented are corrosive. This means that some of the fittings must be made of corrosion-proof material. Plastic can be used for many things, but where pressure and sunlight are involved, then stainless steel may be needed. Again, as the gas is corrosive due to the presence of hydrogen sulfide and other impurities, it may have to be collected in a stainless steel tank in some cases. The cost for such materials is high and may be prohibitive, but larger industrial systems will be forced to go in this direction to get a useful working life. Stainless steel is not inexpensive, but it has properties that make its use essential in various applications.

The level of carbon dioxide and proportion of methane provide valuable information about the state of the fermentation process. [Infrared sensors](#) are the best means employed today for this purpose. The need for calibration is minimal or nonexistent and the small size, relatively low cost and minimal power consumption make them ideal for this type of application. Infrared sensors come in the more expensive two channel variety or the more popular single channel sensor. Whilst more prone to drift, single channel sensors are usually more than adequate for this task. Measurements of carbon dioxide and methane in biogas have, nevertheless, shown a marked deviation from the behavior of an ideal gas, with the sum of the calculated partial pressures not equaling the total pressure. The result of these [measurements](#) must be taken into

account in all cases where both sensors are employed. Accurate monitoring of pH and temperature is also critical.

Biogas Refining & Renewable Ammonia Production

A typical modern ammonia-producing plant first converts natural gas (i.e., methane) or LPG (liquified petroleum gases such as propane and butane) or petroleum naphtha into gaseous hydrogen. The method for producing hydrogen from hydrocarbons is referred to as "Steam Reforming." Methane-rich biogas can be utilized in place of natural gas. Additionally, methane feeds for high temperature fuel cells allow for cogeneration of 1200 lbs of H₂ per day per MW of DG-CHP produced. The hydrogen is then combined with nitrogen to produce ammonia. In the latter case, the production of hydrogen from biomethane can be skipped, but hydrogen sulfide still needs to be removed from biogas.

Starting with a natural gas or biogas feedstock, the processes used in removing sulfur and producing the hydrogen are:

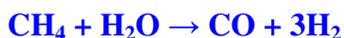
The first step in the process is to remove sulfur compounds from the feedstock because sulfur deactivates the catalysts used in subsequent steps and also contaminates fuel cell stacks when biomethane is utilized as a feed for high temperature fuel cells. Sulfur removal requires catalytic hydrogenation to convert sulfur compounds in the feedstocks to gaseous hydrogen sulfide. In organic chemistry, R-SH is a thiol compound (R) that contains a functional group composed of a sulfur atom and a hydrogen atom (-SH). For refining methane-rich biogas, hydrogen sulfide is already in gaseous form, hence this step can be skipped:



The gaseous hydrogen sulfide is then absorbed and removed by passing it through beds of zinc oxide where it is converted to solid zinc sulfide.



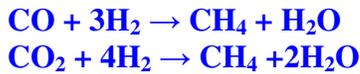
Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide. For H₂ cogeneration via high temperature fuel cells using methane-rich biogas feeds, the following hydrogen production and carbon dioxide removal steps are skipped:



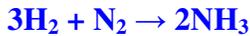
The next step requires catalytic shift conversion or water-gas shift reaction to convert the carbon monoxide to carbon dioxide and more hydrogen:



The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media. The final step in producing the hydrogen is to use catalytic methanation to remove residual amounts of carbon monoxide or carbon dioxide from the hydrogen gas:



To produce the desired end-product ammonia, hydrogen is catalytically reacted with inert nitrogen (N_2 derived from process air which is almost 80% nitrogen) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the [Haber-Bosch](#) process):



The steam reforming, water-gas shift conversion, carbon dioxide removal and methanation steps each operate at absolute pressures of about 25 to 35 bar, and the ammonia synthesis loop operates at absolute pressures ranging from 60 to 180 bar depending upon which proprietary design is used. There are many engineering and construction companies that offer proprietary designs for ammonia synthesis plants. Haldor Topsoe of Denmark, Uhde GmbH of Germany, and Kellogg Brown & Root of the US are among the most experienced companies in this field.

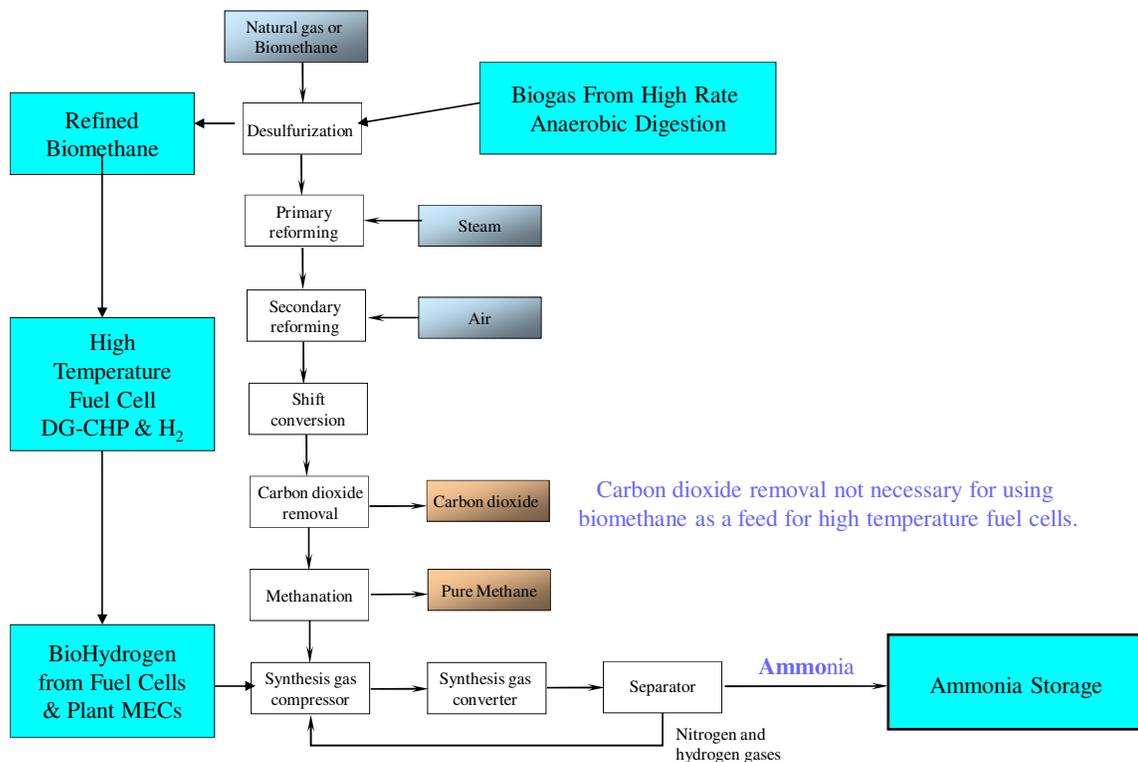


Figure 10. Basic Ammonia Production Process (steam reforming) & Integration of Anaerobic Digestion, Fuel Cells & Plant MECs which Provide Biohydrogen

Ammonia as a Hydrogen-Rich Energy Carrier

The low volumetric energy density of hydrogen—in both compressed gas and liquid forms—makes the storage of hydrogen a difficult problem for most applications. This limitation is felt

most strongly in the area of onboard storage, but it is also problematic in the delivery and distribution of hydrogen. Hydrogen's low energy density is perhaps one of the greatest barriers to the implementation of hydrogen fueled fuel cell vehicles.

Ammonia has several desirable characteristics that suggest its use as a medium to store hydrogen. First, it can be liquefied under mild conditions. The vapor pressure of ammonia at room temperature is 9.2 bar (~121 psig). Its physical properties are similar to those of propane (see Table below). This means that ammonia can be stored in a simple, inexpensive pressure vessel. Second, ammonia has a large weight fraction of hydrogen. Hydrogen constitutes 17.65% of the mass of ammonia. When these two factors are combined, the result is a liquid that is simply contained, with a volumetric hydrogen density about 45% higher than that of liquid hydrogen. Ammonia can be decomposed (cracked) over a catalyst to produce the desired fuel—hydrogen (H₂) along with nitrogen (N₂) a non-toxic, non-greenhouse gas.

In addition, ammonia might be an excellent transition fuel. It can be burned directly in an internal combustion engine (ICE) with no carbon emission, converted to electricity directly in an alkaline fuel cell, or cracked to provide hydrogen for non-alkaline fuel cells (FC). Central production from hydrocarbon fuels (e.g., natural gas) would provide opportunities for CO₂ capture; transportation and distribution would be simpler and cheaper than hydrogen delivery; and final use in an internal combustion engine or fuel cell would produce no carbon dioxide.

Ammonia Properties

Hydrogen Content					
H2 weight fraction	17.65	wt. %	H2 volume density	0.105	kg/liter
Solid Phase					
Melting point	-78	°C	Latent heat of fusion (1 atm at triple point)	-337.37	kJ/kg
Liquid Phase					
Vapor pressure (21°C)	8.88	bar	Liquid density (1atm @ boiling point)	682	kg/m ³
Boiling point (@ 1.0 atm)	-33.5	°C	Liquid/gas equivalent (1 atm and 15°C)	947	vol/vol
Latent heat of vaporization (1 atm @ boiling point)	1371.2			kJ/kg	
Critical temperature	132.4	°C	Critical pressure	112.8	bar
Gas Phase					
Gas density (1 atm at boiling point)	0.86	kg/m ³	Gas density (1 atm at 15°C)	.73	kg/m ³
Compressibility (Z) (1 atm at 15°C)	.9929		Specific gravity (air=1) (1 atm at 20°C)	.597	
Specific volume 1 atm at 20°C)	1.411	m ³ /kg	Viscosity	.000098	Poise
Heat capacity at constant pressure (Cp) (1 atm at 15°C)	.037	kJ/(mol.K)	Heat capacity at constant pressure (Cv) (1 atm at 15°C)	.028	kJ/(mol.K)

Critical Density:	0.24	g/ml	Entropy, Gas @ 25°C., 1 atm. :	45.97	cal/mol°C
Thermal conductivity	22.19			mW/(mK)	
Misc					
Water solubility (1 atm at 0°C)	862	vol/vol	Autoignition temperature	630	°C
Lower flammable limit in air	15%	by volume	Upper flammable limit in air	28%	by volume
Molecular Weight:	17.03				

Ammonia Electrolysis Cells (AEC)

Problems associated with hydrogen sources and storage, and limitations in fuel flexibility are delaying the commercialization of fuel cells as a competitive technology for both transportation and stationary applications.

Ammonia is an effective hydrogen-rich energy carrier for efficiently storing and transporting hydrogen. In conjunction with producing ammonia for \$300/metric tonne and using MCFC or solar power inputs costing \$0.214/kWh, producing hydrogen via ammonia hydrolysis requires 95% less energy and is 71% less costly to produce than using water electrolysis. Renewable electricity can be produced for \$0.07/kWh. Ammonia electrolysis is 8.2% less costly than producing hydrogen via natural gas reforming. Ammonia hydrolysis also has potential for use in wastewater treatment/remediation processes ([Botte, 2006](#)).

Ammonia is an ideal fuel feed for high temperature solid oxide fuel cells (SOFCs) which can cogenerate hydrogen. As with most fuel cells, H₂S needs to be reduced in order to avoid sulfur poisoning of fuel cell stacks. This can be accomplished by optimizing efficiency of digestion and removing residual H₂S in biogas via adsorbent beds or other means. Ammonia SOFC technology reduces production costs by using ceramic materials and simplifies operation of fuel cells. Direct use of NH₃ as a feed eliminates costly fuel processing equipment. SOFCs operate at higher temperature ranges (650-1,000 °C) than either MCFCs or PAFCs, and are generally more efficient than other fuel cell designs. Higher operating temperatures eliminate the need for using precious metal catalysts and capital intensive reforming for a variety of fuel feeds ([Patel & Petri, 2006](#)).

The Electrochemical Engineering Research Laboratory at Ohio University is working on the development of a new technology that can help confront all the issues mentioned above. The technology is called "[Ammonia Electrolysis](#)" and the electrochemical cell is called "Ammonia Electrolytic Cell (AEC) (Botte et al., 2003; Botte, 2004; Vitse et al., 2005)

The AEC operates as follows: aqueous ammonia (NH₃/H₂O) in the presence of potassium hydroxide (KOH) is fed into the anode compartment of the AEC where NH₃ is oxidized in the presence of OH⁻ according to:



At the cathode KOH solutions are supplied and water is reduced in alkaline medium according to:



Therefore, the overall reaction is represented by the following:



The theoretical voltage for the production of hydrogen at 25 °C through electrolysis of ammonia in alkaline media is 0.058 V with an energy consumption of 1.55 W-h per gram of H₂ produced. KOH is the electrolyte for the system and water acts as the solvent, that is, neither KOH nor water are consumables during the operation of the cell.

The advantages of utilizing AEC technology are:

- Low operating temperature. Maximum temperature about 60 °C.
- Could operate with proton exchange membrane (PEM) fuel cells as a power source. Part of the energy of the PEM fuel cell can be used to power the AEC with still net energy left. See [Ammonia Shoe-Sized Car](#) as example.
- Potential use in residential houses due to low operating temperature. See [Self-Sustainable-Ammonia-Power Houses](#) project.
- Easy to operate with renewal energy sources (solar and wind energy)
- Could be extended to use ammonia from waste (e.g., farmers, waste water, etc). See [Farm of the Future](#) project.
- Hydrogen is produced on demand.
- The infrastructure for ammonia distribution and storage is already available.

([Ohio State University, 2008](#))

Round Trip Energy Efficiency Using Ammonia Electrolysis

These types of hydrogen energy based systems provide sustainable and renewable energy. Hydrogen is produced from water versus petroleum or natural gas resources. The Stuart Island Energy Initiative ([Stuart Island Energy Initiative](#)) has built a complete, closed-loop system: Solar panels power an electrolyzer which makes hydrogen. The hydrogen is stored in a 500 gallon tank at 200 PSI, and runs a ReliOn fuel cell to provide full electric back-up to the off-the-grid residence. The SIEI website gives extensive technical details.

Round Trip Energy Efficiency for Distributed Power Generation

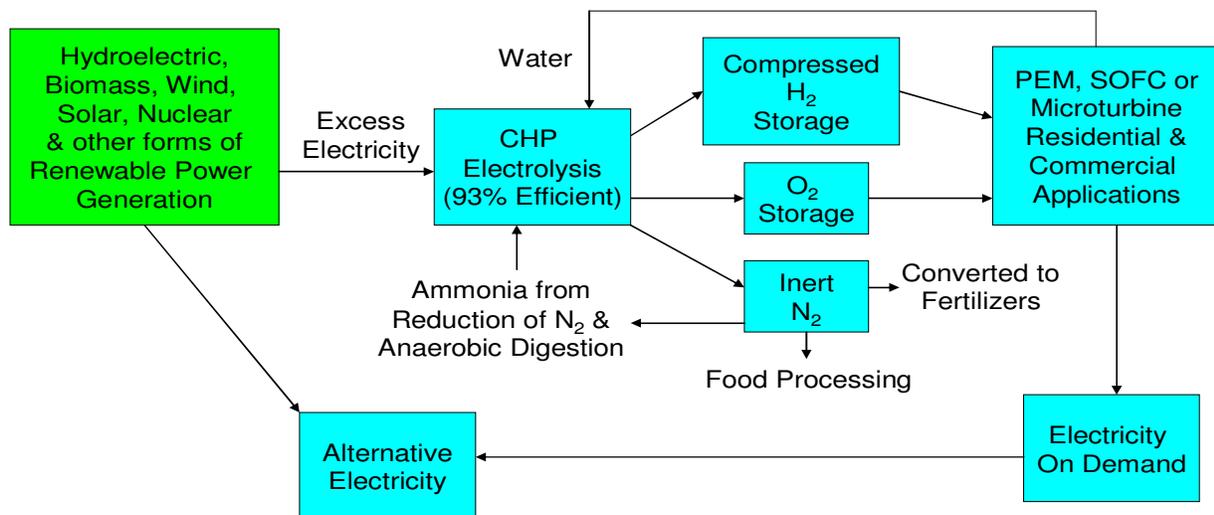


Figure 11. Alternative Electricity on Demand Innovative H₂, O₂ & N₂ Storage Systems

As efficiency of electrolysis and hydrogen-oxygen storage technologies continue to improve, there are exciting opportunities for developing residential and commercial applications of these sustainable technologies with unprecedented efficiencies of operation.

Scientists are currently experimenting with metal hydride storage systems. They are also developing large and efficient electrolyzers that run on DC power and that do not have warm-up periods. Electrolyzers from [Avalence](#) produce hydrogen at over 5,000 psi without compressors via operation under accumulating pressure. This rapidly advancing technology cuts the costs of point-of-use hydrogen production by up to 50%.

Ammonia SOFCs also reduce production costs and simplify operation of fuel cells. Direct use of NH₃ as a feed eliminates costly fuel processing equipment ([Patel & Petri, 2006](#)).

Utilizing Biocatalysts for Increasing Anaerobic Digestion Efficiency & Reducing BOD

“As part of an STTR Phase I grant from NASA, Bruce Rittmann and a team of researchers performed a set of experiments to rigorously test the effects of the OrTec biocatalyst on anaerobic digestion of organic solids.

While the results here are specific to the model system studied, the general trends should be relevant to other types of organic wastes and biological treatment approaches. The anaerobic biodegradation studies rigorously documented that the OrTec biocatalyst had these benefits when it was applied at about 0.5 ppm:

- The hydrolysis of organic solids was systematically enhanced during anaerobic treatment. Without mixing, 0.5-ppm OrTec increased solids removal from 57 to 60%, while the increase was from 67 to 72% with agitation.
- The formation of methane was enhanced to a large degree by 0.5 ppm OrTec during anaerobic treatment. Without mixing, the increase was 44%, while it was 22% with

agitation. The increase in methane generation was associated with greater biodegradation of acetate.

- OrTec at 0.5 ppm gave a large decrease in scum formation in the no-agitation experiments, where scum formation is more likely to occur.
- These beneficial impacts were due to interactions of the OrTec biocatalyst with the normal microbial community. OrTec did not cause significant changes in the anaerobic microbial community and did not act as a biocide.
- The OrTec biocatalyst increased the rate of hydrolysis of organic solids, stimulated the activity of acetate-fermenting methanogens, and broke up scum.

These benefits appear to be related to the following mechanisms;

- hydrolytic enzymes or other materials that enhance the activity of native hydrolytic enzymes
- surfactants
- micro-nutrients that stimulate the activity of methanogens

ORTEC Ltd. produces and markets the OrTec biocatalyst, a natural biological product that consists of five main components that function synergistically to improve the performance of biological treatment of organic solids, wastewater, and gaseous wastes, as well as to control undesired biofilm. These components are:

- Enzymes that hydrolyze organic solids and facilitate the transport of soluble organics into active cells
- Fatty acids that favor the growth of methanogens and the methanogenic breakdown of organics
- Biosurfactants that complex organics, particularly helping the breakdown of fats and oils and also minimizing foaming and odor release
- Mineral nutrients needed for microbial growth
- Chelating agents that keep the inorganics in suspension and prevent scaling

Prior to the research reported here, ORTEC Ltd. had obtained preliminary experimental results that indicated that the OrTec biocatalyst improved biodegradation rates of aerobic and anaerobic bacterial cultures, minimized the reduction of sulfate to hydrogen sulfide, minimized the release of ammonia, and controlled undesired biofilms. Typically, only a small concentration (~ ppm) of the OrTec biocatalyst was required.

Here, we document that the OrTec biocatalyst significantly improved the performance of an anaerobic microbiological process treating a slurry of organic solids. In particular, the rate of solids destruction and the generation of the valuable degradation end product – methane gas – increased when OrTec biocatalyst was added to the influent at only 0.5 ppm. The OrTec biocatalyst increased the rate and extent of the two key reactions in anaerobic microbiological treatment: solids hydrolysis and methane generation by almost 25% (Rittmann et al., 2005).

High Temperature Fuel Cells

MCFCs can provide CHP needed for organic waste and biomass pretreatment processes via integrated biorefineries approaching 90% total energy efficiency. CHP applications allow for using waste heat for thermal integration, thereby eliminating heating costs for thermophilic

digesters. For integrated operations which feed WDG and fermentation residues, each animal unit (AU) produces enough manure to generate 65-100 standard cubic feet (SCF) of biogas. Depending on quality of organic waste substrate, biogas consists of 60-80% methane, 19-39% carbon dioxide, and 1-3% hydrogen sulfide (H₂S) and ammonia/ammonium. Economical biogas refining is available for separating CH₄ from CO₂ and H₂S for use in high temperature fuel cells. This allows for closed loop production at integrated biorefineries in addition to grid connected power generation.

High temperature MCFCs which utilize methane rich feeds (at least 60% biomethane and 40% or less CO₂) are commercially available for DG-CHP applications, providing close to 90% total energy efficiency for innovative applications ([EERE News, DOE, 2008](#)). Cogeneration of H₂ is possible for MCFC applications via integration of proton exchange membrane (PEM) technology. Some states such as California and those with high electricity rates such as Hawaii, provide economic incentives which make installation of high temperature fuel cells and renewable energy applications commercially viable for integrated operations.

Fuel Cell Energy's DFC-3000 produces 2.8 MW of power generation based on 20.2 MBTU/hr fuel feed and 47% electric efficiency. With CHP configurations, 90% total energy efficiency in comparison with fuel inputs is possible for integrated operations. The fuel input requirements is equivalent to 7.21 MBTU/hr fuel feed per MW of power generation. This includes 3.074 MBTU/hr of thermal heat recovery for each MW of power generated ([DFC3000 Brochure, FuelCell Energy, 2008](#)).

For configurations which incorporate proton exchange membrane (PEM) technology for H₂ cogeneration, electric efficiency is reduced to 37% for the same amount of fuel. For MCFC-H₂ units, 7.21 MBTU/hr fuel feed would produce .8 MW of power generation, 1200 lbs/day of H₂, and 1.34 MBTU of heat recovery per MW of power generation for thermal integration.

Internal combustion engines (ICEs) including those used to combust biogas produced by anaerobic digestion are less than 23% electric efficient. A substantial improvement over ICEs is the energy efficiency of high temperature fuel cells which simultaneously provide heat (for provision of process steam, heating anaerobic digesters and providing space heat for CEA) and power generation. This is commonly referred to as combined heat and power (CHP). Molten carbonate fuel cells (MCFCs) utilizing methane rich feeds provide 47% electric efficiency based on biogas consisting of at least 60% methane. CO₂ and H₂S can be economically removed from biogas via state-of-the-art biofiltration or refining technologies in order to insure long term operation of the fuel cell. By incorporating heat recovery via CHP applications for integrated operations, total energy efficiency can theoretically approach 90% for innovative MCFC applications. In addition, if proton exchange membrane (PEM) technology is utilized, MCFCs can provide cogeneration of H₂.

Each megawatt (MW) of power produced by MCFCs can produce about 1,200 lbs of H₂ on a daily basis via proton exchange membrane (PEM) configurations. There is a 20% reduction in CHP applications for cogeneration of H₂. In addition to future conversion of CO₂ to ethanol via hydrogenation, CO₂ derived from fuel cell exhaust and refining biogas can be utilized today for closed loop production of biomass and replenishing oxygen (O₂) in our atmosphere via CEA

applications. Oxygen is required by advanced forms of life. Oxygen can also be utilized to enhance efficiency of electrochemical processes utilized by hydrogen fuel cells. In the near future, high temperature fuel cells such as solid oxide fuel cells (SOFCs) will utilize either biogas or syngas to generate biopower while simultaneously providing DG-CHP for integrated biorefineries.

Both sensible and latent heat recovery allows for achieving unprecedented energy efficiencies via integration of biorefineries and closed loop production. CO₂ and carbonic acid from heat exchangers which utilize condensation can be utilized along with CO₂ from fermentations, anaerobic digestion, and refining of biogas for adding value to production of biomass and ethanol. Latent heat can be utilized as space heat along with providing CO₂ for enriching air, and carbonic acid for enriching both water and air. This results in increasing biomass production by over 62% for C3 carbon fixation plants via photosynthesis ([Bushway and Pritts, 2002](#)). GHGEs are essentially eliminated, providing revolutionary advances in renewable energy efficiency for integrated biorefineries and bioenergy complexes which simultaneously produce biofuels, bioproducts and bioenergy via closed loop production.

Matrixes for calculating total energy efficiency consisting of electric efficiency and thermal heat recovery reveal the following:

90% total energy efficiency, 60% electric efficiency with rankine heat engine

$(1.0 \text{ MWhr} \times 3.415 \text{ MBTU}) / 5.692 \text{ MBTU} = .60$ electric efficiency

$0.90 \text{ total energy efficiency} = (1.0 \text{ MW} \times 3.415 \text{ MBTU} + X \text{ MBTU/hr}) / 5.692 \text{ MBTU/hr input}$

Solving for X = $(0.90 \times 5.692) - (1.0 \times 3.415) = 1.7078 \text{ MBTU/hr}$

90% total energy efficiency, 47% electric efficiency w/o rankine heat engine

$(1.0 \text{ MWhr} \times 3.415 \text{ MBTU}) / 7.21 \text{ MBTU} = .47$ electric efficiency

$0.90 \text{ total energy efficiency} = (1.0 \text{ MW} \times 3.415 \text{ MBTU} + X \text{ MBTU/hr}) / 7.26 \text{ MBTU/hr input}$

Solving for X = $(0.90 \times 7.21) - (1.0 \times 3.415) = 3.074 \text{ MBTU/hr}$

The primary advantages of using electrochemical conversion technology of fuel cells over thermal combustion processes of coal and natural gas turbines are the increases in total energy efficiency for CHP applications. It is considerably more energy efficient to produce heat as a byproduct of power generation than visa versa. Though rankine heat engines can utilize thermal integration via high temperature fuel cells to produce additional power, for integrated biorefineries this source of heat may be more efficiently utilized to provide process steam for biorefining. Fuel cells also provide dramatic reductions in GHGEs and air pollution. For fuel cells operating on 99.9% pure biomethane or ethanol feeds, NO_x emissions are essentially eliminated. In a comparison of high temperature fuel cells operating at 90% total energy efficiency with conventional natural gas or coal CHP systems operating at 49% total energy efficiency ([CHP for the Ethanol Industry, EPA](#)), GHGEs are reduced by over two fold. EPA provides a list of [state incentives and funding opportunities for CHP](#) applications.

In Jul 2009, DOE announced that a solicitation will seek applications for funding of research, development and demonstration of stationary CHP systems at three power levels. The first level covers "large" systems with greater than 20 megawatts (MW) of electricity output. This area has an estimated total budget of \$30 million—\$15 million from the DOE. Area 2 has an estimated

total budget of \$30 million—\$15 million in federal funding and covers "medium" size systems between 1 MW and 20 MW. Area 3 has an estimated budget of \$20 million—\$10 million in DOE cost-share—and covers "small" size systems under 1 MW.

All levels will seek applications that provide plans to perform research and development focused on increasing the efficiency and reducing GHGEs of stationary CHP systems. These systems will be able to replace or reduce natural gas usage as well as minimize the energy and cost penalties of meeting emission regulations. The [Industrial Technologies Program](#) (ITP), part of the Office of Energy Efficiency and Renewable Energy, is DOE's lead organization for CHP Research and Development.

For closed loop production of biomass and biofuels via integrated biorefineries which process organic waste and recycle CO₂, carbonic acid (produced during heat recovery using condensers) and NO_x emissions via CEA applications (which provide CO₂ enrichment), energy costs and total GHGEs are essentially eliminated.

In comparison with other prime movers, additional advantages of fuel cell power plants are provision of uninterrupted power, stability to the grid via DG power contribution, and reduction of electric efficiency losses via DC power output. Fuel cells are best suited for providing base-load power needs, but with hybridization can also support peak power needs. The [Emergency Economic Stabilization Act of 2008 \(Section 103\)](#) and the Economic Stimulus Acts of 2009 provide Investment Tax Credits (ITC) of \$3,500/kW up to 30% of capital costs for fuel cell applications. Emissions Reduction Credits (ERCs) are also available for fuel cell applications in some states such as CA, providing an investment credit of \$200,000 per 300 kW of power generation in comparison with combustion technologies. A list of ITCs, ERCs, and [Renewable Energy Certificates \(RECs\)](#) available for each state is available via the [Database of State Incentives for Renewable Energy \(DSIRE\)](#).

CO₂ is produced during fermentation, during anaerobic digestion, combustion processes, and in the exhaust of high temperature fuel cells which utilize biomethane and bioethanol feeds. For example, a 100 MGY ethanol biorefinery annually produces 468,900 tonnes of CO₂ from fermentation alone. Generally speaking, for each tonne of ethanol produced, a tonne of CO₂ is also produced. Utilizing this for CO₂ enrichment in conjunction with nutrient rich fertigation streams for CEA can increase biomass production by over 62%. Based on producing 1.9 tonnes of biomass from each tonne of CO₂ that is recycled results in annual production of 890,910 tonnes of biomass. Based on production of 125 gal/tonne of lignocellulosic biomass, this would result in production of an additional 111 MGY of ethanol. Based on 60% oil content of algal biomass and 90% extraction, this would result in production of 138 MGY of biodiesel and either 44.5 MGY ethanol or 356,364 tonnes of starch-protein meal for use in livestock feedstuffs.

In addition to processing animal waste, the relatively high protein and lipid content of animal offal from slaughter/packing processes and lignin-free cellulose content of algal biomass can potentially increase quantity and quality of biogas production by 2-3 fold. The maximum estimate for biogas produced per AU is based on daily production of 100 SCF at 80% methane from animal waste via state-of-the-art animal waste collection, pretreatment, and thermophilic HSAD technology. This is equivalent to producing 29 MBTU per AU. However, average biogas

production per AU is currently only 10 MBTU. This is due primarily to inefficient collection of animal waste followed by inadequate processing. In addition to processing animal waste, mixed substrates high in lipid concentrations such as animal tallow, carbohydrates from food processing waste, offal and algal biomass can produce biogas containing as much as 82% methane (Busch et al., 2009) with 93% methane recovered (Cirne, et al., 2006) via thermophilic anaerobic digesters (Angelidaki et al., 1990).

As an alternative to conventional yeast fermentations which produce ethanol, a two-stage process has been developed consisting of an open hydrolysis treatment of solids followed by treating liquids in a fixed-bed methane reactor. The process allows for efficient destruction of biomass and food processing waste, however the hydrolysis process can require 5-18 days followed by 18-20 hours of hydraulic retention time in the methane reactor. Residues from industrial processes such as glycerine wastewater resulting from biodiesel production can also be efficiently converted to biogas. However, the process is not designed to process animal waste. The process is extremely stable and has been continuously operating without interruption since inception. The open hydrolysis stage releases 50% of CO₂ and allows for oxidation of sulfur. Consequently, the biogas is rich in methane concentrations (72%-82%). Open access to air or oxygen during the hydrolysis stage results in an oxidation of sulfur to sulfates which reduces H₂S to less than 100 ppm. Hence, the methane-rich biogas is ideal for using as a feed for high temperature fuel cells. Stirrers or other agitation equipment are not necessary since only liquids are pumped. The two stage process allows for efficiently manipulating the quality and composition of biogas (Busch et al., 2009).

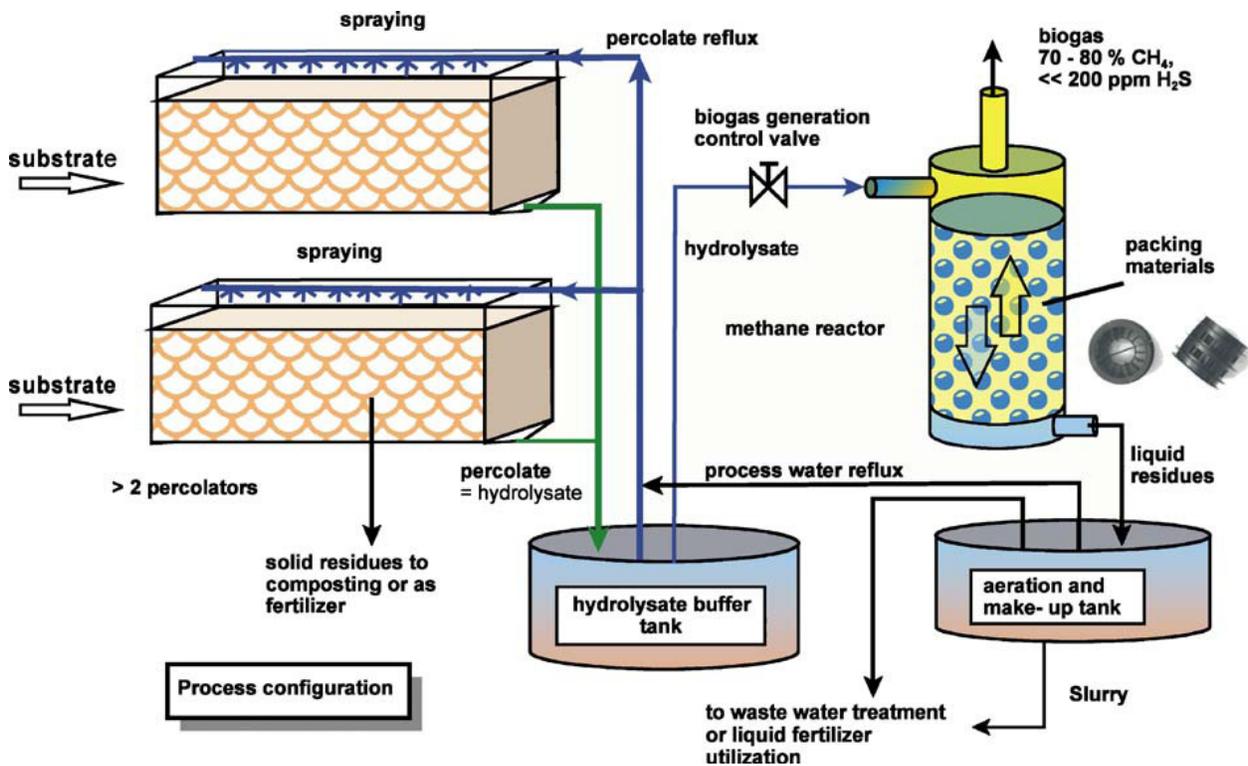


Figure 12. Two-Stage Hybrid Reactor Producing 80% Methane Concentrations

With 90% of energy inputs at a typical ethanol plant coming from natural gas or coal, displacing these fossil fuels with renewable biomethane could capture over \$6 million per year in carbon credits and premiums for producing ethanol at 50 MGY biorefinery.

With the demand for price-volatile natural gas expected to increase 66% over the next 25 years, biomass and biogas energy is a long-term, physical hedge that an ethanol producer can implement to manage risk. Using biogas can also help to reduce an ethanol producer's carbon footprint and help to keep more money in the local economy. There are multiple sources of funds available to assist with financing. It's possible that these operations can be funded primarily with government money and very little equity.

Federal funding options include an "open-loop" biomass investment tax credit that can be used to recover 30% of capital costs and a combined heat and power (CHP) investment tax credit can be used to recover 10%. There are also closed loop investment tax credits available and a new market tax credit available to capture \$2 million for every \$10 million in capital expenditures. For loan guarantees, the US DOE offers 100% loan guarantees on 20% equity and the USDA offers loan guarantees of up to \$25 million. The Rural Energy for America program offers up to \$25 million in loan guarantees or \$500,000 grants, and has money available for completing feasibility studies. There is also the opportunity to depreciate the assets over five years and many states have additional incentives available ([Biomass Magazine, Jun 2009](#)). Federal incentives are also available for replacing gas-turbine combustion systems with innovative high temperature fuel cells that provide distributive generated combined cooling heating and power (DG-CCHP) and operate on refined biogas or biomethane feeds as described above.

In addition to providing process heat which comprises 92% of total energy consumption for conventional dry mill ethanol plants, the electrical power requirement (8%) is .75 kWhr/gal of ethanol ([Mueller and Cuttica, 2007](#)). This is equivalent to requiring 8.6 MW per 100 MGY for conventional ethanol production. Based on reducing electrical power requirements for integrated biorefineries to 5 MW per 100 MGY of ethanol produced, up to 86% of the power produced, (e.g. 32 MW per 100 MGY) from animal waste and food processing waste can be sold to the local power grid. CHP providing 90% total energy efficiency provides sufficient process steam and heat for closed loop systems which simultaneously produce biofuels, bioenergy, food, biochemicals and bioproducts. Closed loop architecture results in reducing or eliminating economic dependence on importing petroleum products.

On June 12, the USDA Rural Business-Cooperative Service published two notices in the Federal Register announcing that funding will be made available for two programs established under Title IX of the 2008 Farm Bill.

One of these programs, the Repowering Assistance Program, is designed to provide payments to biorefineries that replace fossil fuel-derived heat and power with renewable biomass heat and power systems. The bill provides a total of \$35 million in funding for fiscal year 2009, and authorized \$15 million of that funding for fiscal years 2009 through 2012. In order to qualify, a biorefinery must have been in existence at the time the 2008 Farm Bill was passed.

Applications for the Repowering Assistance Program are being accepted between July 1 and November 1. “There is a window of opportunity for biorefinery entities that have an interest in retooling to bring on a biomass energy source versus a fossil fuel energy source to make application,” said Bill Hagy, deputy administrator of business programs rural development with the USDA Rural Business-Cooperative Service. The program is competitive. Procedures and criteria for applying are detailed in the [notice of funding](#) that was published in the Federal Register.

The [second notice](#) published in the Federal Register announced the intent of the USDA to enter into contracts to make payments to Eligible Advanced Biofuel Producers to support and ensure an expanding production of Advanced Biofuels. According to the notice, in order to participate in the program during fiscal year 2009, applications must be received between June 12 and August 11. “What’s unique about this program is there is no competition for entities that apply that are determined to be eligible,” Hagy said. “Any entity that applies that is determined to be eligible that is producing an advanced biofuel and that meets the other criteria of the notice of contract proposal will get a portion of the \$30 million that is available. That will be divided up among the eligible applicants based on their amount of production.”

For more information on programs established under Title IX of the 2008 Farm Bill, refer to the [USDA website](#).

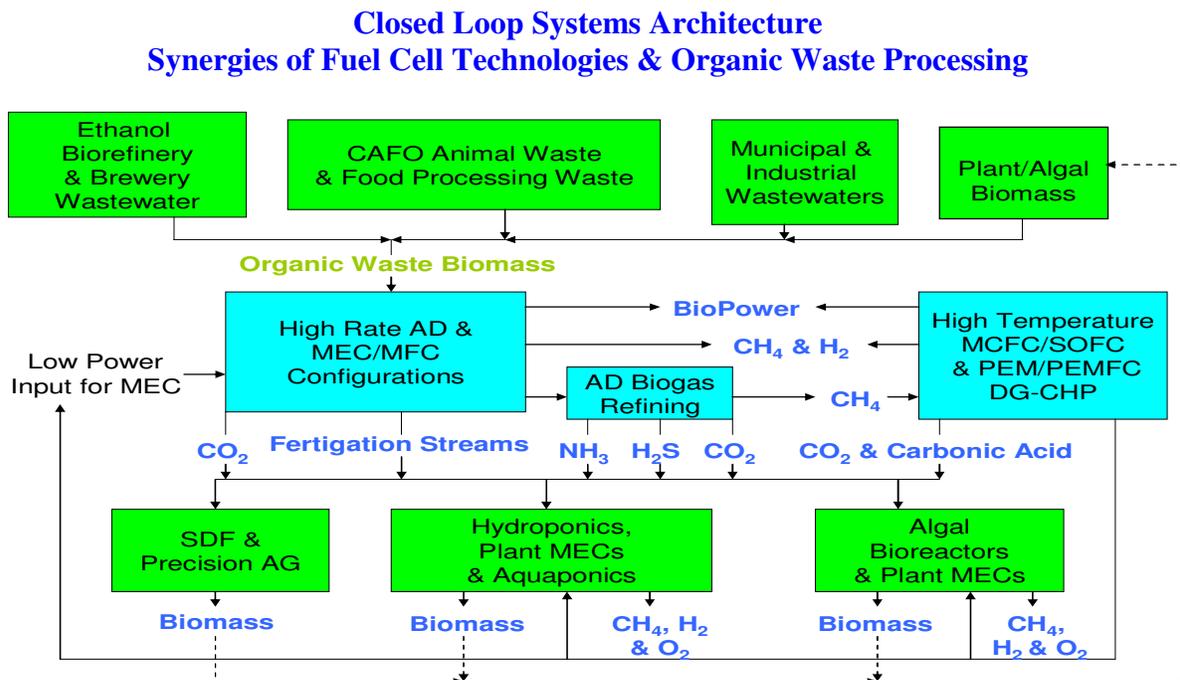


Figure 13. Closed Loop Production of BioPower, Biogas & Biomass

References

American Public Health Association. 1960. Standard Methods for the Examination of Water and Wastewater. 11 ed. New York.

- Anderson, S. 1957. Farm Manure. U. S. Dept. Agriculture, Yearbook of Agric. 1957: 229-257.
- Angelidaki, I., S. P. Petersen and B. K. Ahring. 1990. [Effects of lipids on thermophilic anaerobic digestion and reduction of lipid inhibition upon addition of bentonite](#). *Applied Microbiology and Biotechnology*, Volume 33, Number 4 / July, 1990.
- Babcock, B.A., and A. M. Blackmer (1994). "The Ex Post Relationship Between Growing Conditions and Optimal Fertilizer Levels," *Review of Agricultural Economics* , Vol. 16, No. 3. Sept.
- Badri, D.V., and J.M. Vivanco. 2009. Regulation and function of root exudates. *Plant, Cell and Environment* (2009) 32, 666–681.
- Bais HP, Weir TL, Perry JG, Gilroy S, Vivanco JM. [The role of root exudates in rhizosphere interactions with plants and other organisms](#). *Annual Review of Plant Biology* 2006; 57:233–266.
- Balsam, J. 2002. Anaerobic Digestion of Animal Wastes: Factors to Consider, available from www.attra.ncat.org (cited 12 March 2007)
- Barkar, U. A. 1956. Bacterial Fermentations. John Wiley & Sons, New York.
- Bates, T.E. 1971. Factors affecting critical nutrient concentrations in plants and their evaluation: A review. *Soil Sci.* 112:116-130.
- Beaufils, E.R. 1957. Research for rational exploitation of Hevea using a physiological diagnosis based on the mineral analysis of various parts of the plants. *Fertilite* 3:27-38.
- Beaufils, E.R. 1971. Physiological diagnosis-A guide for improving maize production based on principles developed for rubber trees. *Fertile. Soc. S. Afr. J.* 1:1-28.
- Beaufils, E.R. 1973. Diagnosis and recommendation integrated system (DRIS). *Soil Science Bull. No.1*, University of Natal, S. Africa.
- Beaufils, E.R., and M.E. Sumner. 1976. Application of the DRIS approach for calibrating soil, plant yield and plant quality factors of sugarcane. *Proc. S. Aji'. Sugar Tech. Assoc.* 50: 118-124.
- Beeson, K.C. and H.A. MacDonald 1951. Absorption of mineral elements by forage plants. III. The relation of stage of growth to the micronutrient element content of timothy and some legumes. *Agron. J.* 43:589-593.

Bosch, Darrell J., Keith O. Fuglie, and Russ W. Keim (1994). "Economic and Environmental Effects of Nitrogen Testing for Fertilizer Management." Staff Report AGES9413. U.S. Dept. Agr., Econ. Res. Serv. April. Botte, G. G.; F. Vitse, and M. Cooper, **"Electrocatalysts for the Oxidation of Ammonia and their Application to Hydrogen Production, Fuel Cells, Sensors, and Purification Processes", Pending Patent, US (2003).**

- Botte, G.G. 2006. [Recovery of Ammonia Energy from Municipal and Agricultural Wastewater: Ammonia Electrolysis](#). Presentation at Ammonia Conference.
- Bouma, D. 1983. Diagnosis of mineral deficiencies using plant tests. In: A. Lauchli and Bielecki, R.L. (eds.) *Elcyclopedia of Plant Physiology*. Vol. 15A. Inorganic Plant Nutritioll. Springer-Verlag, Berlin, pp. 120-146.
- [Biodesign Institute, Arizona State University, 2008](#)
- Busch, G., J. Großmann, M. Sieber & M. Burkhardt. 2009. [A New and Sound Technology for Biogas from Solid Waste and Biomass](#). *Water Air Soil Pollut: Focus* (2009) 9:89–97.

- Cecava, M.J., N.R. Merchen, L.L. Berger, and G.C. Fahey, Jr. 1990. Intestinal supply of amino acids in sheep fed alkaline hydrogen peroxide-treated wheat straw-based diets supplemented with soybean meal or combination of corn gluten meal and blood meal. *J. Anim. Sci.* 68:467-477.
- Cecava, M.J. and J.E. Parker. 1993. Intestinal supply of amino acids in steers fed ruminally degradable and undegradable crude protein sources alone and in combination. *J. Anim. Sci.* 71:1596-1605.
- Chastain, J.P., Linvill, D.E. and Wolak, F.J. 1999. [On-Farm Biogas Production and Utilization for South Carolina Livestock and Poultry Operations.](#)
- Cheng, S., D. Xing, D. Call, and B.E. Logan. 2009. [Direct biological conversion of electrical current into methane by electromethanogenesis.](#) *Environ. Sci. Technol.* In Press, published online 26 Mar 2009.
- [Cheng, S., and B.E. Logan. 2007b.](#) Sustainable and efficient biohydrogen production via electrohydrogenesis. *PNAS*, 104(47): 18871–18873.
- Cheng, S., D. Xing, D.F. Call and B.E. Logan. 2009. [Direct Biological Conversion of Electrical Current into Methane by Electromethanogenesis.](#) *Environ. Sci. Technol.*, 2009, 43 (10), pp 3953–3958.
- [Chicago Climate Exchange \(CCX\)](#)
- Cirne, D.G., X. Paloumet, L. Björnsson, M.M. Alves and B. Mattiasson. 2007. [Anaerobic digestion of lipid-rich waste—Effects of lipid concentration.](#) *Renewable Energy* Volume 32, Issue 6, May 2007, Pages 965-975.
- Coomer, J.C., H.E. Amos, M.A. Froetschel, K.K. Ragland, and C.C. Williams. 1993. Effects of supplemental protein source on ruminal fermentation, protein degradation, and amino acid absorption in steers and on growth and feed efficiency in steers and heifers. *J. Anim. Sci.* 71:3078-3086.
- Cuéllar, A.D. and Webber, M.E. 2008. [Cow power: the energy and emissions benefits of converting manure to biogas.](#) *Environ. Res. Lett.* 3 (July-September 2008) 034002, doi:10.1088/1748-9326/3/3/034002.
- Cundiff, Larry. 2007. Phone conversations with MARC-USDA beef cattle geneticist, Larry Cundiff.
- Cundiff, L.V., Szabo, F., Gregory, K.E., Koch, R.M., Dikeman, M.E., and Crouse, J.D. [Breed Comparisons in the Germplasm Evaluation Program at MARC.](#) 1993. ARS, USDA, Presented at the Beef Improvement Federation 25th Anniversary Conference, May 26-29, 1993, Asheville, NC; <http://www.ansi.okstate.edu/breeds/research/marccomp.htm>
- Davis, J.G., D.B. Bosley, R. Buhler, and A.W. Cooley. 1999. Comparison of soil testing laboratories. p. 93-99. In T. Tindall and D. Westermann (eds) Proc. of the Western Nutrient Management Conference, March 4-5, 1999. Salt Lake City, Utah.
- Dorfner, Konrad (Ed.) 1991. Ion Exchangers. Walter de Gruyter Berlin. 1495pp.
- Dugan, Gordon L. et. al. 1970. Photosynthetic Reclamation of Agricultural Solid & Liquid Wastes. Sanitary Engineering Research Laboratory, University of California at Berkeley SERL Report no. 70-1.
- [E3 Regeneration Solutions](#)
- Echternkamp, S.E., R.M. Thallman, R.A. Cushman, M.F. Allan and K.E. Gregory. 2007. [Increased calf production in cattle selected for twin ovulations;](#) *J. Anim. Sci.* 2007. 105:3239-3248. doi:10.2527/jas.2007-0210; <http://jas.fass.org/cgi/content/abstract/85/12/3239>

[EIA USDOE: Biomass for Electricity Generation](#)

- Erisman, J.W., M.A. Sutton, J. Galloway, Z. Klimont and W. Winiwarer. 2008. [How a century of ammonia synthesis changed the world](#). *Nature Geoscience*, Vol 1, pages 636 – 639.
- Feng, Y., Wang, X. Logan, B.E., and Lee, H. 2008. [Brewery wastewater treatment using air-cathode microbial fuel cells](#). *Applied Microbiology and Biotechnology*, 0175-7598 (Print) 1432-0614 (Online)
- Fry, L.J. 2009. [Methane Digesters For Fuel Gas and Fertilizer](#)
- Gattrell, M., N. Gupta and A. Co. 2007. [Electrochemical reduction of CO2 to hydrocarbons to store renewable electrical energy and upgrade biogas](#). *Energy Conversion and Management*, Volume 48, Issue 4, April 2007, Pages 1255-1265.
- Ghose, T.K., A. Singh and S.N. Mukhopadhyay. 1979. [Increased methane production in biogas](#). *Biotechnology Letters*, Volume 1, Number 7/July 1979, pages 275-280.
- Ghose, T.K. and S.N. Mukhopadhyay. 1976. *Ind. Chem. Engr.*, 18, 12.
- Gotaas, H. 1956. *Composting: Sanitary Disposal and Reclamation of Organic Wastes*. World Health Organization, Geneva.
- Gregory, K.E., S. E. Echternkamp, G. E. Dickerson, L. V. Cundiff, R. M. Koch and L. D. Van Vleck. 1990. [Twinning in cattle: I. Foundation animals and genetic and environmental effects on twinning rate](#). Roman L. Hruska U.S. Meat Anim. Res. Center, ARS, USDA, Clay Center, NE 68933; *Journal of Animal Science*, Vol 68, Issue 7 1867-1876; <http://jas.fass.org/cgi/content/abstract/68/7/1867>
- Gunaseelan, V.N. 2009. [Biomass estimates, characteristics, biochemical methane potential, kinetics and energy flow from *Jatropha curcus* on dry lands](#). *Biomass and Bioenergy* Volume 33, Issue 4, April 2009, Pages 589-596.
- Hammond, C. 2005. *Animal Waste and the Environment*. <http://www.engr.uga.edu/service/extension/publications/c827-cd.html>
- Hart, Samuel. 1960. *Sludge Digestion Tests of Livestock Manures*. Dept. Agr. Engr. Univ. of Calif. Davis. Offprint manuscript.
- Hart, S. 1963. *Fowl Fecal Facts: National Symposium on Poultry Foul Wastes*, Lincoln American Society Agricultural Engineers, University of Nebraska.
- Heck, A. 1931. *The Availability of the Nitrogen in Farm Manure under Field Conditions*. *Soil Sci.* 31: 467:481.
- Hill, D.T. 1991. Steady-state mesophilic design equations for methane production from livestock wastes *Trans. ASAE* 34 2157–63, [Order from Infotrieve](#).
- [Huang, L. and B.E. Logan. 2008a](#). Electricity generation and treatment of paper recycling wastewater using a microbial fuel cell. *Appl. Microbiol. Biotechnol.* 80(2)349-355.
- Huang, L., and B.E. Logan. 2008b. [Electricity production from xylose in fed-batch and continuous-flow microbial fuel cells](#). *Appl. Microbiol. Biotechnol.* 80(4) September
- Ingles, C. 2006. [Manure, nutrient planning pays for small farms](#). <http://extension.agron.iastate.edu/waterquality/neidpmaterials/ww87-1.html>
- Jitaru, M. [Electrochemical carbon dioxide reduction- fundamental and applied topics](#) (Review). *J. Univ. Chem. Technol. Metall.* 2007, 42, 333–344.
- Kellogg, R.L., Lander, C.H., Moffitt, D.C. and Gollehon, N. 2000. [Manure Nutrients Relative to the Capacity of Cropland and Pastureland to Assimilate Nutrients: Spatial and Temporal Trends for the United States](#). USDA-NRCS Website.
- Kerely, Monty. 2007. Phone conversations regarding data from feed trials, Animal Science Dept., University of Missouri, phone: (573) 882-0834; email: KerleyM@missouri.edu;

- Feed conversion ratios decreased by over 20% from 5.9 to 4.8 for enhancing diet formulations for beef cattle.
- Kim, J.-R., J. Dec, M.A. Bruns, and B.E. Logan. 2008b. Removal of odors from swine wastewater by using microbial fuel cells. *Appl. Environ. Microbiol.* 74(8):2540-2543.
- KITCO. 24 h platinum spot chart. <http://www.kitco.com/market/> (accessed Sept 24, 2008).
- [King County Fuel Cell Demonstration Project](#)
- Kirkpatrick, B.W. 2002. [Management of Twinning Cow Herds](#). Department of Animal Sciences, University of Wisconsin, Madison 53706; *J. Anim. Sci.* 80 (E. Suppl. 2):E14–E18; <http://www.asas.org/jas/symposia/esupp2/jas1401.pdf>
- Klein, S. 1972. Anaerobic Digestion of Solid Wastes. *Compost Science Jour.* Feb. 1972.
- Koenig, R.T. 2003. Certification of soil testing labs. P 83-87. In J. Ellsworth (eds) Proc. of the Western Nutrient Management Conference, March 6-7, 2003. Salt Lake City, Utah.
- Kramer, D.A. 2004. [Nitrogen, Mineral Commodity Profiles](#). USGS, Dept of Interior.
- Lansing S, Botero R B and Martin J F 2008 Waste treatment and biogas quality in small-scale agricultural digesters *Bioresource Technol.* **99** 5881–90
[CrossRef Link](#) | [Order from Infotrieve](#)
- Liu, H., Cheng, S., Huang, L., Logan, B.E. [Scale-up of membrane-free single-chamber microbial fuel cells](#). *Journal of Power Sources* 179 (2008) 274–279
- Liu, H.; Cheng, S.; Huang, L.; Logan, B. E. [Scale-up of membrane free single-chamber microbial fuel cells](#). *J. Power Sources* 2008, 179 (1), 274–279.
- Logan, B. E. Extracting Hydrogen and Electricity from Renewable Resources. *Environ. Sci. Technol.* 2004, 38, [160A-167A](#).
- Lorbeer, S., S. Schaff, and J. Jacobsen. 1999. A comparison of soil test lab results and recommendations. p. 101-106. In T. Tindall and D. Westermann (eds). Proc. of the Western Nutrient Management Conference, March 4-5, 1999. Salt Lake City, Utah.
- Ludden, P.A. and M.J. Cecava. 1995. Supplemental protein sources for steers fed corn-based diets: I. Ruminant Characteristics and Intestinal amino acid flows. *J. Anim. Sci.* 73:1466-1475.
- Management of Farm Animal Wastes. 1966. Proc. National Symposium on animal waste management. May 5-7, 1966. East Lansing Mich. From: American Society of Agricultural Engineers. St. Joseph, Mich. 49085 (\$5.00)
- McCarthy, R.D., T.H. Klusmeyer, J.L. Vicini, J.H. Clark, and D.R. Nelson. 1989. Effects of source of protein and carbohydrate on ruminal fermentation and passage of nutrients to the small intestine of lactating cows. *J. Dairy Sci.* 72:2002-2016.
- McSwiney, C. P., and G. P. Robertson. 2005. [Non-linear response of N₂O flux to incremental fertilizer addition in a continuous maize \(*Zea mays* sp.\) cropping system](#). *Global Change Biology* 11: 1712-1719;
- [MEPS](#). World Stainless Steel Prices. <http://www.meps.co.uk/Stainless%20Prices.htm> (accessed Sept 24, 2008).
- [Microbial Fuel Cell Organization, 2008](#)
- Miller, R.O., J. Kotuby-Amacher, and N. B. Dellavalle. 1996. A proficiency testing program for the agricultural laboratory industry: results of 1994 program. *Com. Soil Sci. Plant Anal.* 27:451-461.
- Miller, R.O. 2006. [A Western Evaluation of Soil Testing Laboratory Performance](#). *Better Crops/Vol.* 90 (2006, No. 1). Formerly the Coordinator of the North American Proficiency Testing Program and Affiliate Professor with Colorado State University, Fort

- Collins, CO 80550; Robert is currently the Technical Director of the Agricultural Laboratory Program, Manure Analysis Proficiency Program Coordinator, and Compost Analysis Proficiency Program Coordinator at Colorado State University.
- Miller, R.O. 2007. Email and phone conversations; Email: rmiller@lamar.colostate.edu; Phone: (970) 686-5702.
- [Min, B. and B.E. Logan. 2004.](#) Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. *Environ. Sci. Technol.* 38(18):4900-4904.
- Mishihara, S. 1935. Digestion of Human Fecal Matter. *Sewage Works Journal.* 7(5): 798-809.
- Mueller, Steffen and John Cuttica. 2007. [Research investigation for the potential use of combined heat and power at natural gas and coal fired dry mill ethanol plants](#); Prepared for U.S. Department of Energy, November, 2007; US DOE Midwest CHP Application Center.
- Mulvaney, R. 2001. [A New Nitrogen Soil Test That Works](#). Dept. of Natural Resources and Environmental Sciences; University of Illinois, Urbana; phone: (217) 333-9467; Email: mulvaney@uiuc.edu; website: <http://agronomyday.cropsci.uiuc.edu/2001/tours/soil-test/index.html>
- Murphy, L. 2007. Phone conversations with soil scientist and consultant Larry Murphy, Murphy Agro, 2805 Claflin Road, Suite 200, Manhattan, KS 66502, 785-776-6623, cell: 785-477-0794, email: murphyagro@sbcglobal.net.
- Murphy, J.D., McKeogh, E. and Kiely, G. 2004. Technical/economic/environmental analysis of biogas utilization *Appl. Energy* 77 407–27
[CrossRef Link](#) | [Order from Infotrieve](#)
- Nielsen, P.H. 2002. [Heat and Power Production from Pig Manure](#) available from <http://www.lcafood.dk/processes/energyconversion/heatandpowerfrommanure.htm> (cited 6 Aug 2009)
- Nkrumah, J. D., E. K. Okine, G. W. Mathison, K. Schmid, C. Li, J. A. Basarab, M. A. Price, Z. Wang and S. S. Moore. 2006. [Relationships of feedlot feed efficiency, performance, and feeding behavior with metabolic rate, methane production, and energy partitioning in beef cattle](#). *J Anim Sci* 84: 145-153.
- Papandros, S. & B. Brown. 1950. Poultry Manure. Connecticut Agric. Exper. Station Bulletin 272.
- Patel, P., and R. Petri. 2006. [Co-production of Electricity and Hydrogen Using NH₃-Fueled SOFC Systems](#). Presented at Ammonia Fuel Conference 2006 Golden, CO, October 9-10, 2006.
- Patel, P., and R. Petri. 2006. [Co-production of Electricity and Hydrogen Using NH₃-Fueled SOFC Systems](#). Presented at Ammonia Fuel Conference 2006 Golden, CO, October 9-10, 2006.
- Patterson, C.A. and W.M. Ingledew. 1999. Utilization of peptides by a lager brewing yeast. *Journal of the American Society of Brewing Chemists*, 57: 1-8.
- Patterson, D. J., D. J. Schafer, and M. F. Smith. 2007. Review of Estrus Synchronization Systems: MGA[®]; Division of Animal Sciences, University of Missouri, Columbia.
- Peck, Clint. [Crossbreeding With Composites](#). Senior editor for Beef Magazine with comments and information provided by Jim Gosey, UN Extension representative for Nebraska beef producers; http://beef-mag.com/mag/beef_crossbreeding_composites

- Pennington, J.A., K. VanDevender, J.A. [Jennings. Nutrient and Fertilizer Value of Dairy Manure](#). Retrieved from the Internet, Aug, 2009, via University of Arkansas Cooperative Extension Service, FSA4017.
- Quaggio J.A., H. Cantarella and B. van Raij. 1994. Evolution of the analytical quality of soil testing laboratories integrated in a sample exchange program. *Commun. Soil Sci. Plant Anal.*, 25, 1007-1014
- Ramsay, Ian R. and Pratap C. Pullammanappallil. 2005. [Full-Scale Application of a Dynamic Model for High-Rate Anaerobic Wastewater Treatment Systems](#). *J. Envir. Engrg.*, Volume 131, Issue 7, pp. 1030-1036 (July 2005)
- [Ren, Z., T. Ward, B.E. Logan, and J.M. Regan. 2007](#). Characterization of the cellulolytic and hydrogen-producing activities of six mesophilic *Clostridium* species. *J. Applied Microbiol.* 103(6): 2258–2266.
- Rezaei, F., T.L. Richard, and B.E. Logan. 2008. [Enzymatic hydrolysis of cellulose coupled with electricity generation in a microbial fuel cell](#). *Biotechnol. Bioengin.* Published Online: 11 Jun 2008.
- Rittmann, B.E., César Torres, Andrew Marcus, Michael Marsolek, Slil Siripong and Alex Schwarz. 2005. Effect of OrTec Biocatalyst Anaerobic, Methanogenic Biodegradation of Organic Solids.
- Rominger, R.S., D. Smith and L.A. Peterson. 1975. Changes in elemental concentrations in alfalfa herbage at two soil fertility levels with advance in maturity. *Comm. Soil Sci. Plant Anal.* 6:163-180.
- Rooke, J.A. and D.G. Armstrong. 1989. The importance of the form of nitrogen on microbial protein synthesis in the rumen of cattle receiving grass silage and continuous intrarumen infusion of sucrose. *Br. J. Nutr.* 61:113
- Rubins, E. and F. Bear. 1942. Carbon-nitrogen Ratios in Organic Fertilizer Materials in Relation to the Availability of their Nitrogen. *Soil Sci.* 54:411-423.
- Salter, R. M. and Schollenberger, C. J. 1939. Farm Manure. Ohio Agricultural Experiment Station Bulletin 605.
- Sanders, F. A. & D. Bloodgood. 1965. The Effect of Nitrogen to Carbon Ratio on Anaerobic Decomposition. *J. Wat. Pollut. Control Fed.* 37:1741.
- Sathianthan, M.A. 1975. In: *Biogas – Achievement and Challenges* AVARS Pub., 5th Edition.
- Schoenau, J.E. 2007. Phone conversations and email correspondence. Saskatchewan Agriculture and Food Research Chair in Nutrient Management Soil fertility, nutrient management. Department of Soil Science College of Agriculture and Bioresources, University of Saskatchewan, Saskatoon, Canada SK S7N 5A8; Phone: (306) 966-6844; FAX: (306) 966-6881; E-mail: schoenau@sask.usask.ca
- Schnabel, C. F. 1973. *Grass. Acres: A Voice Eco-Agriculture*, March 1973. Box 1456, Kansas City, Mo. (A monthly newspaper of high quality.)
- Shortle, J.S., W.N.Musser, W.C. Huang, B. Roach, K. Krehling, D. Beegle, and R. M. Fox (1993). Economics of Environmental Potential of the Pre-side-dressing
- Singh, Ram Bux. 1971a. Bio-Gas Plant. Gobor Gas Research Station. Ajitman, Etawah (U.P.) India.
- Singh, Ram Bux. 1971b. Some Experiments with Bio-Gas. Gobor Gas Research Station, Ajitman, Etawah (U.P.) India.

- Skogley, E.O. 1994. Reinventing soil testing for the future. p. 187-201. **In** J.L. Havlin et al., (ed) Soil testing: Prospects for improving nutrient recommendations. Soil Sci. Soc. Am. Spec. Publ. 40, ASA and SSSA, Madison WI.
- Skogley, E.O. 2007. Phone conversations with soil scientist Earl Skogley, founder of UNIBEST, Inc.; 3535 Stucky Rd., Bozeman, MT, 59718; phone: 406-587-4630; fax (406) 587-4870; email: eskogley@montana.com ; website: www.unibest.us
- Skogley, E.O., A. Dobermann, G.E. Warrington, M.F. Pampolino, and M.A. Adviento. 1996. [Laboratory and field methodologies for use of resin capsules](#). Sciences of Soils Vol.1.
- Skogley, E.O. and A. Dobermann. 1996. Synthetic ion-exchange resins: Soil and environmental studies. *J. Environ Qual.* 25:13-24.
- Skogley, E.O., A. Dobermann, J.E. Yang, B.E. Schaff, M.A.A. Adviento and M.F. Pampolino. 1997. [Methodologies for Resin Capsules: Capsule Storage and Ion Recovery](#), SCIENCES of SOILS, Rel. 2, 1997; <http://www.hintze-online.com/sos/1997/Articles/Art3>
- Sobel, A. 1966. Physical Properties of Animal Associated with Handling, In "Management of Farm Animal Wastes;" Proceedings National Symposium on Animal Waste Management.
- Sumner, M.E. , 1985. The diagnosis and recommendation integrated system (DRIS) as a guide to orchard fertilization. Leaf Diagnosis as a Guide to Orchard Fertilization, Food & Fert. Tech. Center for Asia and Pacific Region, Suweon, Korea.
- Tafdrup, S. 1995. Viable energy production and waste recycling from anaerobic digestion of manure and other biomass materials *Biomass Bioenergy* 9, 303–14
[CrossRef Link](#) | [Order from Infotrieve](#)
- Taiganides, Eliseos P. 1963. Characteristics and Treatment of Wastes from a Confinement Hog Production Unit. PhD dissertation, Iowa State Univ. Science and Technology, Agricultural Engineering. Available from University Micro-film Inc. Ann Arbor, Mich. #63-5200, 177 pp.
- Taiganides, E. P. 1963. Anaerobic Digestion of Poultry Manure. *World's Poultry Science Journal* 19(4).
- Taiganides, E. P., E. Baumann, H. Johnson, T. Hazen. Anaerobic Digestion of Hog Wastes. *Journal Agricultural Engin. Research* 8(4).
- Takahashi, J., and B.A. Young. 2002. Greenhouse Gases and Animal Agriculture. Editors. New York, NY: Elsevier Science, 2002, 372 pp. ISBN: 0-444-51012-5.
- Thoney, M.L. [Economic Simulation of Twinning vs. Single Calving Programs](#). Dept. of Animal Science, 114 Morrison Hall, Cornell University, Ithaca, NY 14853-4801, phone (607) 255-2851, email mlt2@cornell.edu,
<http://www.ansci.cornell.edu/courses/as360/lab/cowherd/budget.xls>
- Titgemeyer, E.C., N.R. Merchen, and L.L. Berger. 1989. Evaluation of soybean meal, corn gluten meal, blood meal and fish meal as sources of nitrogen and amino acids disappearing from the small intestine of steers. *J. Anim. Sci.* 67:262-275.
- US DOE EIA, 2007 Annual Energy Outlook 2007 With Projections to 2030 EIA Department of Energy Editor
[US EPA, 2006 Electricity from Natural Gas](#)
[US EPA, 2009, Methane Sources and Emissions](#)
[US EPA Air Emissions Inventory 2005](#)
[US EPA CHP Partnership; Municipal Wastewater Treatment Facilities](#)
[USDA Economic Research Service 2001](#)

- Vitse, F.; M. Cooper; and G. G. Botte, "[On the Use of Ammonia Electrolysis for Hydrogen Production](#)," *J. Power Sources*, 142, 18 (2005).
- Waksman, S. 1938. *Humus: Origin, Chemical Composition and Importance in Nature*. Williams & Wilkins Co., Baltimore.
- Walters, D. T. 2006. [Fertilizer nitrogen source and management impacts on greenhouse gas emissions](#). University of Nebraska, Lincoln, Nebraska.
- Walters, D. T. 2006. [Fertilizer nitrogen source and management impacts on greenhouse gas emissions](#). University of Nebraska, Lincoln, Nebraska.
http://soilfertility.unl.edu/Materials%20to%20include/Research%20Pubs/Walters_Fertilizer%20nitrogen%20source%20and%20management%20impacts%20on%20greenhouse%20gas%20emissions.pdf
- Walworth, J.L., and M.E. Sumner. 1987. *The Diagnosis and Recommendation Integrated system*. Advances in Soil Science, Volume 6. Springer-Verlag, New York, Inc.
- Walworth, J.L., and M.E. Sumner. 1988. Foliar diagnosis: A review. *Adv. Plant Nutr.* 3:193-241
- Wilkie, A.C. 2006. [Farm in Alachua producing bio-gas made from animal waste](#). Article by Chuck Woods quotes Anne Wilkie.
- Wilkie, A.C. 2007. *Anaerobic Digestion Found to Produce Renewable Energy*, Hague, Florida. Article quotes Anne Wilkie.
- [Xing, D., Y. Zuo, S. Cheng, J.M. Regan, and B.E. Logan. 2008.](#) Electricity generation by *Rhodospseudomonas palustris DX-1*. *Environ. Sci. Technol.* 42(11): 4146-4151.
- Yang, J.E., E.O. Skogley, S.J. Georitis, B.E. Schaff, and A.H. Ferguson. 1991. The Phytoavailability Soil Test: Development and verification of theory. *Soil Sci. Soc. Am. J.* 55:1358-1365.
- Yang, J.E., E.O. Skogley. 1992. Diffusion Kinetics of Multinutrient Accumulation by Mixed-Bed Ion-Exchange Resin. *Soil Science Society of America Journal* 56:408-414.
- [Zuo, Y., D. Xing, J.M. Regan, and B.E. Logan. 2008a.](#) Isolation of the exoelectrogenic bacterium *Ochrobactrum anthropi YZ-1* by using a U-tube microbial fuel cell. *Appl. Environ. Microbiol.* 74(10):3130-3137.